

American University in Cairo

## AUC Knowledge Fountain

---

Theses and Dissertations

---

2-1-2020

### Sustainable treatment of tanneries wastewater using low-cost and highly efficient materials

Sarah Ehab Abdelkader

Follow this and additional works at: <https://fount.aucegypt.edu/etds>

---

#### Recommended Citation

##### APA Citation

Abdelkader, S. (2020). *Sustainable treatment of tanneries wastewater using low-cost and highly efficient materials* [Master's thesis, the American University in Cairo]. AUC Knowledge Fountain.

<https://fount.aucegypt.edu/etds/810>

##### MLA Citation

Abdelkader, Sarah Ehab. *Sustainable treatment of tanneries wastewater using low-cost and highly efficient materials*. 2020. American University in Cairo, Master's thesis. *AUC Knowledge Fountain*.

<https://fount.aucegypt.edu/etds/810>

This Thesis is brought to you for free and open access by AUC Knowledge Fountain. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of AUC Knowledge Fountain. For more information, please contact [mark.muehlhaeusler@aucegypt.edu](mailto:mark.muehlhaeusler@aucegypt.edu).



**THE AMERICAN UNIVERSITY IN CAIRO**  
**School of Sciences and Engineering**

**SUSTAINABLE TREATMENT OF TANNERIES  
WASTEWATER USING LOW-COST AND HIGHLY  
EFFICIENT MATERIALS**

By

**Sarah Ehab Nagaty Abdelkader**

A thesis submitted in partial fulfillment of the requirements for the  
degree of Master of Science in Environmental Engineering

Under Supervision of:

**Dr. Ahmed El-Gendy**  
**Associate Professor, Department**  
**of Construction Engineering,**  
**The American University in Cairo**

**Dr. Salah El-Haggar**  
**Professor, Department of**  
**Mechanical Engineering,**  
**The American University in**  
**Cairo**

**August 2019**

## Abstract

Chromium sulfate salt ( $\text{Cr}_2(\text{SO}_4)_3$ ) is the tanning agent used in the chrome tanning process, but during the process around 30 or 40% of the chromium is discharged as chromium III residues in the tannery's wastewater resulting in serious health and environmental problem in case of discharging to the environment without appropriate treatment. The main objective of this study is to investigate the efficiency of using solid waste materials for low-cost trivalent chromium removal from tanneries wastewater. This study was conducted in 5 phases: phase I, phase II, phase III, phase IV and phase V. In phase I, two groups of waste materials, organic and inorganic waste materials, were tested for the removal of trivalent chromium from aqueous solution and the results indicated that the group of inorganic waste materials, including marble powder (MP) and cement bypass kiln dust (CKD), showed better removal efficiency of chromium III. In phase II, the optimum mixing conditions, best removal efficiency and the energy required in the treatment process for both MP and CKD were studied. The results indicated that CKD showed better removal efficiency and lower energy consumption. In phase III, CKD was selected to carry further investigation on the treatment performance, operating conditions and the mechanisms for the removal of trivalent chromium. In phase IV, real samples wastewater was collected from a tannery in Egypt and it was tested for chromium III removal using CKD under the mixing and operating conditions obtained in phases II and III. The results recorded removal efficiency of chromium III of 99.97%. Finally, in phase V, chromium III recovery from the precipitated sludge using sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were studied. The best chromium III recovery efficiency was found to be 96.13 % using 7.75%  $\text{H}_2\text{SO}_4$  solution and sludge dose of 2.5g.

## Acknowledgment

I want to express my deep thanks to everyone who helped and supported me to complete this work. Firstly, I need to give special thanks for my advisors Dr. Ahmed El-Gendy and Dr. Salah Elhaggar for their unlimited help and support during this work. Also, I need to express my thanks to Eng. Ahmed Saad, environmental engineering laboratory instructor, and Mohamed Mostafa, environmental engineering laboratory lab aide for their help and guidance during laboratory work. In addition, I need to thank Eng. Yasser Shaaban Akl from the Center of Leather Tanning Technology for helping during my visit to tanneries in Old Cairo or in Al-Robeky City. Also, my deep thanks should be given to my friend Dr. Yasmine Abdel-Maksoud for helping me in getting the CKD samples and for her technical help.

In addition, I need to express my deep gratitude for my dear mother for all her endless support and help in my motherhood responsibilities during my work and for her prayers. I also need to thank my brother and sister for their help and guidance. In addition, my deep thanks should be given to my dear daughter Emy for being my strongest motivate to finish this work.

Finally, I need express my deep thanks for my friends Eng. Sherif Zaher, Eng. Alaa Abbas, Eng. Israa El-Mitainy, Eng. Mohammed Osman, Manar Elnaggar, Monira Yazied, Youssef Abdel-Raouf and Amal Abul-Fetouh for all the support and help during this work.

## LIST OF ABBREVIATIONS

Cr III	Trivalent chromium
Cr VI	Hexavalent chromium
CKD	Cement bypass kiln dust
$G_{fm}$	Flash mixing speed or velocity gradient
$G_{gm}$	Flocculation (gentle) mixing speed or velocity gradient
E	Energy consumed due to mixing
P	Power consumed due to mixing
t	Time
$K_T$	Impeller constant
n	Rotational speed
$D_i$	Impeller diameter
$W_i$	Impeller width
$\rho$	Water Density
$N_{Re}$	Reynolds Number
$\mu$	Water absolute viscosity
C	Cr III concentration per gram of precipitate
$C_0$	Initial concentration of Cr III in the solution
$C_f$	Final concentration in the supernatant
V	Volume of the Solution
m	Mass of the precipitated sludge

# TABLE OF CONTENTS

Abstract .....	i
Acknowledgment .....	ii
LIST OF ABBREVIATIONS .....	iii
TABLE OF CONTENTS .....	iv
LIST OF TABLES .....	viii
LIST OF FIGURES .....	ix
Chapter 1: Introduction .....	1
1.1 Industrial Wastewater Problem in Egypt .....	1
1.2 Solid waste Problem in Egypt .....	2
1.3 Heavy Metals Contamination .....	4
1.3.1 Chromium .....	5
1.4 Problem Statement .....	7
1.5 Objectives .....	7
Chapter 2: Literature Review .....	8
2.1 Leather Industry Processes .....	8
2.1.1 Beam House Stage .....	9
2.1.2 Tanning Stage .....	10
2.1.3 Post-Tanning Stage .....	10
2.2 Tanning Wastewater Characteristics .....	11
2.3 Treatment Methods .....	14
2.3.1 Conventional Tanneries Wastewater Treatment .....	15
2.3.2 Other Treatment Methods for Chromium Removal .....	16
2.4 Chemical Precipitation Treatment Method .....	19
2.4.1 Chemical Precipitation Types .....	20

2.4.2 Chemical Precipitation for Chromium Removal from Tannery Wastewater ..	22
2.5 Solid Wastes for Low-Cost Treatment .....	23
2.5.1 Rice Straw .....	23
2.5.2 Rice Husk.....	24
2.5.3 Sugarcane Bagasse.....	24
2.5.4 Sawdust .....	25
2.5.5 Cement bypass kiln dust .....	26
2.5.6 Marble Powder.....	26
2.6 Chromium Recovery.....	27
Chapter 3: Materials and Methods.....	28
3.1 General.....	28
3.2 Phases of Study .....	28
3.3 Phase I: Solid wastes Comparative Study.....	29
3.3.1 Preparation of Solid Waste Materials for Phase I Experiments.....	29
3.3.2 Preparation of Synthetic Solution for Phase I Experiments.....	30
3.3.3 Experimental Set up of Phase I Experiments.....	30
3.4 Phase II: Effect of Mixing Conditions on the Removal of Cr III .....	31
3.4.1 Preparation of Synthetic Solution for Phase II Experiments .....	32
3.4.2 Experimental Setup for Phase II .....	32
3.4.3 Energy Consumption Calculations .....	34
3.4.4 Velocity Gradient Calculations.....	35
3.5 Phase III: Identifying Optimum Operating Conditions .....	36
3.5.1 Phase III - Part I: Effect of CKD dose and Cr III initial concentration .....	36
3.5.2 Phase III - Part II: CKD Versus Reference Precipitants for the Removal of Cr III.....	37
3.6 Phase IV: Testing of Real Tannery wastewater .....	38

3.6.1 Properties of Tannery Wastewater .....	38
3.6.2 Experimental procedure .....	38
3.6.3 Characterization of the Precipitated Sludge.....	39
3.7 Phase V: Chromium Recovery from Precipitates due to Treatment.....	39
3.7.1 Phase V - Part I: Effect of Reaction Time .....	39
3.7.2 Phase V - Part II: Effect of H <sub>2</sub> SO <sub>4</sub> Concentration on Recovery .....	40
3.7.3 Phase V - Part III: Effect of the percentage of Sulfuric Acid Volume to the Weight of the Sludge .....	41
3.8 Trivalent Chromium Analysis Method Using Flame Atomic Absorption Spectrometry .....	42
Chapter 4: Results and Discussion.....	43
4.1 Performance of Different Waste Materials .....	43
4.1.1 Material Selection According to Wastes Performance .....	46
4.2 Identifying Flocculation mixing speed (G <sub>sm</sub> ) and Material Dose .....	46
4.2.1 Visual Effect of the CKD and MP Doses .....	46
4.2.2 Effect of Flocculation mixing speed .....	48
4.3 Effect of Mixing on the Performance of Cement bypass kiln dust (CKD) and Marble Powder (MP) in Chromium Removal .....	49
4.3.1 Cement bypass kiln dust .....	51
4.3.2 Marble Powder (MP) .....	54
4.4 Comparison Between Cement bypass kiln dust (CKD) and Marble Powder According to Energy Consumption Due to Mixing.....	57
4.5 Comparison Between the Performance of Cement bypass kiln dust and Marble Powder in Chromium Removal under different Mixing Conditions .....	59
4.6 Effect of CKD dose and Cr III initial concentration.....	60
4.7 Mechanism of Removal of Cement bypass kiln dust.....	64



4.7.1 Cement bypass kiln dust (CKD) and Magnesium Oxide (MgO) Removal Efficiencies .....	64
4.7.2 Effect of Increasing pH values Using Cement bypass kiln dust (CKD) and Sodium Hydroxide (NaOH) on the Removal Efficiency .....	66
4.7.3 General Discussion on Mechanism of Removal .....	69
4.8 The Performance of the Treatment Technique on Real Sample of Tanneries Wastewater.....	71
4.9 Efficiency of Chromium Recovery from the Precipitated Sludge Using Sulfuric Acid .....	73
4.9.1 Effect of Reaction Time in the Chromium Recovery Process .....	74
4.9.2 Effect of Sulfuric Acid Concentration on the Chromium Recovery Efficiency .....	75
4.9.3 Effect of Percentage of H <sub>2</sub> SO <sub>4</sub> Volume to the Weight of the Sludge on the Recovery Efficiency of Chromium III.....	78
4.9.4 Chemical Composition of the Resulted Sludge from Chromium III Recovery Process and Regeneration .....	81
Chapter 5: Conclusion and Recommendations .....	83
5.1 Conclusion .....	83
5.2 Recommendations.....	86
References .....	87
Appendix.....	94

## LIST OF TABLES

Table 1–1: Generated Solid Wastes (2001-2012) (Zaki et al., 2013) .....	3
Table 2–1: Pollution Loads for Each of Tanning Processes (Ludvik, 2000).....	13
Table 2–2: Pressure-driven Membrane Separation Processes (Kocurek et al., 2015) .....	19
Table 4–1: Phase I experimental results .....	44
Table 4–2: $G_{fm}$ Pretest Results for CKD and MP .....	49
Table 4–3: Important Parameters.....	50
Table 4–4: $G_{fm}$ and $G_{gmt}$ values results for CKD: .....	52
Table 4–5: $G_{fm}$ and $G_{gmt}$ values results for MP .....	55
Table 4–6: Removal efficiency and Total energy for CKD and MP .....	58
Table 4–7: CKD doses and Cr III initial concentrations results .....	61
Table 4–8: CKD and MgO Results .....	65
Table 4–9: CKD and NaOH Results .....	68
Table 4–10: Chemical Analysis of CKD .....	69
Table 4–11: Chemical Composition of the precipitated sludge (synthetic Solution) .....	70
Table 4–12: CKD Doses Tested for Tanneries Wastewater Treatment.....	71
Table 4–13: Effect of CKD Treatment on Tanneries Wastewater Characteristics .....	72
Table 4–14: Chemical Composition of the precipitated sludge (Tannery Wastewater) ...	74
Table 4–15: Phase V results (Part I) .....	75
Table 4–16: Phase V Results (Phase II).....	77
Table 4–17: Phase V Results (Part III) .....	79
Table 4–18: Optimum Conditions for chromium III Recovery .....	80
Table 4–19: Chemical Composition of the Resulted Sludge from the Recovery Process..	81

## LIST OF FIGURES

Figure 1.1: Solid Wastes Breakdown in Egypt in 2012.....	3
Figure 1.2: Examples of Heavy Metals.....	4
Figure 2.1: Inputs and Outputs of Tanning Processes .....	12
Figure 2.2: Effluents Percentages for Tanning Stages.....	14
Figure 2.3: Schematic Diagram for Primary Treatment Stage .....	15
Figure 2.4: Schematic Diagram for Secondary Treatment Stage .....	16
Figure 2.5: Metal Hydroxides Solubility Curves (Hoffland Environmental Inc., 2017)..	21
Figure 3.1: Labeled High Density Polyethylene Bottles .....	30
Figure 3.2: HDP Bottles on the mechanical orbital .....	31
Figure 3.3: Experimental Variables in Phase II.....	32
Figure 3.4: Schematic Diagram for the Impeller Used in the phases II, III and IV.....	35
Figure 4.1: Solid Wastes Removal Efficiencies .....	44
Figure 4.2: Final pH values for treated solutions.....	45
Figure 4.3: Rice Straw and Cement bypass kiln dust Treatment.....	46
Figure 4.4: Cement bypass kiln dust Residue.....	46
Figure 4.5: Effect of 1g CKD on the Color of the Solution.....	47
Figure 4.6: Effect of MP dosages on the Color of the Solution.....	47
Figure 4.7: Flocculation mixing speed ( $G_{gm}$ ) vs. Removal Efficiency for CKD and MP (initial pH = 3.00) .....	49
Figure 4.8: Removal Efficiencies for $G_{fm}$ and $G_{gm} t$ Values (initial pH= 3.00) .....	53
Figure 4.9: pH values vs. $G_{fm}$ and $G_{gm} t$ (CKD) (initial pH= 3.00) .....	54
Figure 4.10: Removal efficiency vs. $G_{fm}$ and $G_{gmt}$ for MP (initial pH= 3.00) .....	56
Figure 4.11: pH values vs $G_{fm}$ and $G_{gm} t$ for (MP) (initial pH= 3.00) .....	57
Figure 4.12: Removal Efficiency % vs. Total Energy (CKD).....	58
Figure 4.13: Removal Efficiency vs. Total Energy (MP).....	59
Figure 4.14: CKD Dose and Cr III initial concentration vs. Removal Efficiency (initial pH= 3.00) .....	62
Figure 4.15: CKD Dose and Cr III initial concentration vs. pH (initial pH= 3.00).....	63

Figure 4.16: pH and Cr III initial concentration vs. Removal Efficiency (initial pH= 3.00)	63
Figure 4.17: Dose vs. Removal Efficiency% for CKD and MgO (initial pH= 3.00)	66
Figure 4.18: Dose vs. pH for CKD and MgO (initial pH= 3.00)	66
Figure 4.19: pH vs. Removal Efficiency for CKD and NaOH	68
Figure 4.20: Removal of Cr III using CKD (left) and NaOH (right)	69
Figure 4.21: Chemical Composition of Raw CKD and precipitated Sludge	70
Figure 4.22: Removal Efficiencies of Different Contaminants	72
Figure 4.23: Effect of Reaction Time on Recovery Efficiency%	75
Figure 4.24: H <sub>2</sub> SO <sub>4</sub> % Vs. Recovery Efficiency %	78
Figure 4.25: v(H <sub>2</sub> SO <sub>4</sub> )/w(sludge) vs. Recovery %	80
Figure 4.26: Chemical Composition of Raw CKD, Precipitated Sludge and Resulted Sludge from the Recovery	82

# Chapter 1: Introduction

## 1.1 Industrial Wastewater Problem in Egypt

According to the minister of planning, the industrial sector represents 20% of the current growth rate of Egypt. In addition, the rate of industrial growth in 18/2019 is 6.8% and the target of the government is to increase this rate to 10% by 21/2022 (Egypt Today, 2019). This information indicates that the industry sector in Egypt is developing and will keep developing during the upcoming period. However, industrial activities have significant environmental impacts affecting freshwater surfaces. Huge amounts of freshwater are used in some industries like petrochemical plants, refinery, food, textile, pharmaceutical and other industries; these amounts of fresh water represented around 10% of the total water use in 2010 and this percentage is expected to increase around 25% by 2025 due to the industrial development (Glavič & Bogataj, 2011). On the other hand, there are huge amounts of wastewater produced due to this industrial development. In Egypt, according to statistics, around 50% of the industries discharge their untreated industrial wastewater into the public sewage network violating the Egyptian environmental regulations (Abou-Elela et al , 2005). In addition, in other statistics, around 400 factories discharge around 2.5 million m<sup>3</sup> of industrial wastewater daily into water surfaces ((Ali et al., 2011) This violation resulted in significant damage in the sewage pipe network and sewage treatment plant; in addition to the dangerous impact of this violation on the freshwater surfaces, human health and aquatic life (Monayeri et al., 2011). Industrial wastewater is considered as a significant source of pollution due to its dangerous chemical and physical characteristics. This kind of wastewater contains high percentages of hazardous materials such as organic contents, toxic chemicals and heavy metals. On the other hand, according to the U.N. World Water Development report for 2018, Egypt is currently below the U.N.'s threshold of water poverty, facing water scarcity and dramatically heading towards absolute water scarcity (WWAP (United Nations World Water Assessment Programme), 2018). So, treating industrial wastewater became a challenge facing Egypt recently not only to minimize the water surfaces pollution but also

to minimize freshwater consumption in industry by reusing the treated wastewater in the industrial activities.

## **1.2 Solid waste Problem in Egypt**

Solid wastes are the undesirable solid materials generated from the different human activities including residential, industrial and commercial activities. These wastes can be categorized according to its nature to organic and inorganic materials, according to its origin into domestic, industrial, agricultural or commercial or according to its hazardousness into toxic, non-toxic, flammable, infectious or radioactive (Moeller, 2019). So, due to the global increase in population and urbanization, solid waste management plays a significant role in sustainable development of the communities. Sustainable solid management is based on integrated solid waste management system which included source reduction, reuse, recycle, waste treatment and landfilling ((Ibrahim & Mohamed, 2016). In Egypt, solid wastes became a chronic problem that faces Egyptian community every day. According to Egyptian Environmental Affairs Agency (EEAA), the total amounts of solid wastes generated in Egypt increased by 24.26% in the period between 2001 to 2012, as shown in Table 1–1, to reach 89.28 million tons per year. According to Figure 1.1, industrial solid wastes represented 6.72% of the total solid wastes generated during 2012, with a 29.17% increase from 2001, and agricultural solid wastes increased by 21.67% to represent 33.6% of the total solid wastes generated during 2012 (Zaki et al., 2013). These amounts are expected to increase due to the increase in the industrial growth rate in Egypt as discussed in the previous section and the increase in the population. According to these facts, investigating new methods for beneficial use of solid wastes became an important action to help the Egyptian community to convert into sustainable community.

Table 1–1: Generated Solid Wastes (2001-2012) (Zaki et al., 2013)

Waste Type	Generated Solid Wastes (Million Tonnes)			Percentage increased
	2001	2006	2012	
Industrial Wastes	4.25	4.75	6	29.17
Medical Wastes	0.12	0.15	0.28	57.14
Waterway Cleansing Wastes	20	30	25	20.00
Municipal Wastes	14.5	17	21	30.95
Construction and Demolition Wastes	3.5	4.6	4	12.50
Agricultural Wastes	23.5	27.5	30	21.67
Sludge	1.75	2	3	41.67
<b>Total</b>	<b>67.62</b>	<b>86</b>	<b>89.28</b>	<b>24.26</b>

### Solid Wastes in Egypt in 2012

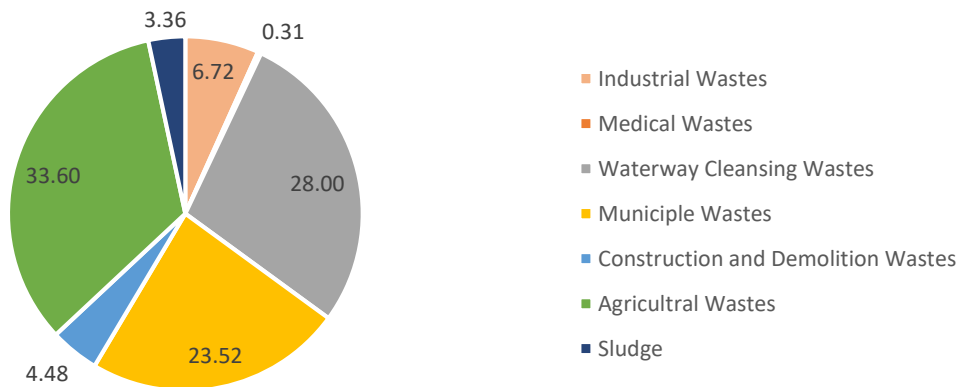


Figure 1.1: Solid Wastes Breakdown in Egypt in 2012

### 1.3 Heavy Metals Contamination

Metals are natural materials found in the earth's crust that tends to donate their electrons to form cations and they have special properties such as high electrical conductivity, malleability and luster (Jaishankar et al., 2014). Heavy metals are the group of metals and metalloids that have high density, compared to water, ranging from 3.5 to 7 g/cm<sup>3</sup> and it includes mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn), nickel (Ni), copper (Cu) and lead (Pb) as shown in Figure 1.2. Although some of these metals are important at very low concentrations for the metabolism and maintaining different bio-chemical and physiological functions in living creatures, they are very toxic and hazardous after exceeding certain concentrations due to their ability to accumulate in the biotic systems (Gautam et al., 2014; Jaishankar et al., 2014). Due to its toxicity and hazardous health effects, heavy metals are considered as hazardous pollutants that can be found in water.

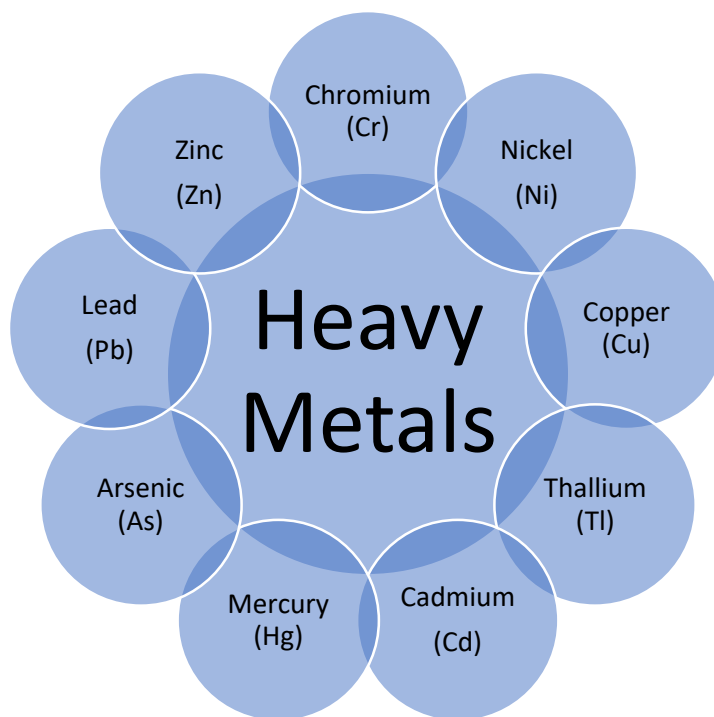


Figure 1.2: Examples of Heavy Metals



### 1.3.1 Chromium

Chromium (Cr) is one of the heavy metals that exists in nature in various oxidation states ranging from chromium (II) to chromium (VI); however, it is stable only in two oxidation states; chromium (III) (Cr III) and chromium (VI) (Cr VI) (Rodríguez et al., 2007). There are differences between these two oxidation states in terms of toxicity, mobility and bioavailability. Cr III is considered as an important nutritional supplement, in certain concentrations, for both humans and animals as it plays a significant role in glucose metabolism; however, high concentrations of chromium (III) resulted in increasing its toxicity and causing harmful health effects. The Egyptian Environmental Law, according to Article 60 and 61 of the Executive Regulations of Law 48, identifies the maximum concentration level for total chromium in the liquid wastes discharged in River Nile and its waterways to be 0.05 mg/l.

#### *1.3.1.1 Industries Using Chromium*

Chromium is considered as one of the important industrial metals due to its properties. Due to its hardness and resistance to corrosion, chromium is used in three main industries which are metallurgical, chemical and refractory industries. Chromium is used widely in stainless steel manufacturing; it prevents corrosion and discoloration of steel. In addition, chromium compounds are used in paints and pigments industries; chromates of barium (Ba), lead (Pb) and zinc (Zn) give the pigments lemon chrome, chrome yellow, chrome red, chrome orange, zinc yellow and zinc green, respectively. These pigments are used in colored glass and paints of automobiles and buildings. Potassium dichromate ( $K_2Cr_2O_7$ ) is used in manufacturing of waterproof glues and in photography and photoengraving (Testa and Jacobs, 2004). In addition, around 90% of raw hides in the world are chrome-tanned using chromium (III) salts that enhance the hydrothermal stability, dying characteristics and softness of leather (Wang, 2019).

#### *1.3.1.2 Environmental and Health Impacts of Chromium*

Chromium is one of the common toxic industrial pollutants which is released to the environment through the industrial effluents and emissions in two oxidation states of Cr (III) and Cr (VI). Cr (VI) is a toxic and carcinogenic form of Cr as it has high oxidizing potential, high solubility, and mobility across the membranes in living organisms and in

the environment (Oliveira, 2012). On the other hand, Cr III has less toxicity, mobility and solubility than Cr (VI) and it is essential for metabolism process in humans and animals in certain concentrations; however, at high concentrations, it accumulates in the animal and human tissues causing DNA damage (Stearns et al., 2018). On the other hand, Cr III can be oxidized to Cr VI by oxidants like peroxides and hypohalite in basic solution in strong oxidation conditions. These conditions can be reached in sterilization process of drinking water. Cr III can reach drinking water by dumping industrial liquid wastes in the rivers and by leaching from industrial wastes from the dumps to the underground water. As a result, during the sterilization process by ozone or hydrochloride, Cr III is oxidized to Cr VI and reacts with magnesium and calcium ions present in the drinking water to form carcinogenic magnesium and calcium chromate or dichromate salts. In addition, there is a possibility of oxidization of Cr III into Cr VI in moderate conditions by air in both acidic and alkaline media (Kolomaznik et al., 2008).

Humans can be exposed to chromium compounds through inhalation, ingestion or skin penetration. Skin penetration is considered as the most significant way of chromium exposure as it is the easiest way for Cr (VI), which is more soluble than Cr (III), to enter the human body and react with the cell membranes causing skin cancer. Cr (VI) poisoning results in acute tubular necrosis of the kidney which is considered as a cause of death. In addition, direct and extensive exposure to chromium compounds results in several diseases including lung cancer, Irritation and damage in the nose, throat and respiratory system, eye and skin rashes, hepatic and renal impairments, and problems in gastrointestinal (Khan et al., 2013; Kolomaznik et al., 2008).

As Cr (VI) forms are extremely soluble under all pH conditions, soil and water can be easily contaminated by chromium. In addition, at high concentrations of oxygen and Mn oxides, Cr (III) can be oxidized to Cr (VI). Cr (VI) affects the enzymatic activity of soils by influencing soil microorganisms and modifying their living environment which is rich by many enzymes. As Cr is taken up by plants through carriers of essential ions such as sulfate, Plants can suffer from Cr toxicity which causes decrease of seed germination, reduction of growth, decrease of yield, inhibition of enzymatic activities, impairment of photosynthesis, nutrient and oxidative imbalances, and mutagenesis (Oliveira, 2012).

## 1.4 Problem Statement

The most important step in the leather industry process is the tanning step. Although there are many types of tanning, around 90% of leather around the world are chrome tanned. Chromium sulfate salt ( $\text{Cr}_2(\text{SO}_4)_3$ ) is usually the tanning agent used in the chrome tanning process, but during the process around 30 to 40% of the chromium is discharged as residues in the tannery's wastewater (Wang, 2019). The process of chrome tanning is considered as a high-water consumption process and it produces around 50 m<sup>3</sup> of wastewater per ton of raw hides with high Chromium (III) concentrations ranging from 3000 to 6000 mg/l (Nashy & Eid, 2018). Although the chromium used in this process is in the trivalent oxidation form, concerns of possible conversion of trivalent state into more toxic hexavalent state under different conditions should be taken in account. In Egypt, the tannery wastewater is discharged directly to the main domestic sewage pipeline which adds difficulties to the sewer system and to the wastewater treatment plant. So, chromium recovery is essential not only for healthy concerns but also for economic and environmental concerns. Since chromium removal process is expensive, there is a need to find a simple and cheap process for removal of chromium from tannery wastewater.

## 1.5 Objectives

Since different waste materials showed potential of metal removal from aqueous solutions, therefore, this study aimed to:

- i. Investigating sustainable tanneries wastewater treatment for chromium removal, in order to be reused in the industry or to be discharged in the environment, using different types of solid wastes.
- ii. Identifying the best suitable material for chromium removal.
- iii. Identifying the best mixing and operation conditions for the best removal efficiency of trivalent chromium.
- iv. Evaluating the efficiency of the treatment technique on real tanning wastewater samples.
- v. Investigating the efficiency of trivalent chromium recovery using sulfuric acid extraction solution.

## Chapter 2: Literature Review

### 2.1 Leather Industry Processes

Leather manufacture is considered as one of the ancient industrial activities in Egypt which was very important for the economy in ancient ages. Ancient Egyptian civilization recorded the first evidences of leather production in the history of humanity. Paintings in the walls of Rekhmire tomb, dated to 1500 B.C, showed the different processes of leather production conducted by leather workers, in addition, there are many different leather products found in other tombs which proved the active leather manufacture at these ages (Elnaggar et al., 2017). Recently, as Egypt has a big wealth of cow hides, sheep and goat skins, known internationally by their high-quality fibrous structure and unique grain pattern, leather industry is considered as an important industrial activity for the economic development in Egypt. More than 300 leather tanneries and around 15,000 workers produce around 150 million of tanned leather annually and 70% of this production is for exporting which makes Egypt the 4<sup>th</sup> highest leather production country after Italy, Spain and Germany within the EU tanning activity (Maher & El-Khair, 2010). After constructing the leather city of Al-Robeky, issuing a decree to protect the Egyptian leather industry, which included reviewing the Egyptian standards for imported leather products and introduced a customs tariff on imported leather products, this industry is tending to improve and scale up in the domestic and international markets (HADDAD, 2018).

According to El-Sabbagh & Mohamed, 2010, Leather is defined as a natural polymer consisting of collagen fibers cross-linked in a three-dimensional structure which gained its appearance, physical, chemical and biological properties through tanning process. Tanning process is defined as the process of converting animal hides and skins into leather through three stages: beam house stage, tanning stage and post-tanning stage (Nazer et al., 2006). These three stages will be discussed in the following sections. It should be noted that the mentioned percentages in the upcoming description is based on the hides weight.

### 2.1.1 Beam House Stage

This stage consists of three processes including soaking, liming and deliming. These processes are pretreatment processes for the hides and skins to be prepared for the tanning stage.

- Soaking

The purpose of this process is to dehydrate the hides and skins in order to remove salt, dirt and blood, and facilitate the removal of non-collagenous proteins during the upcoming stages. During this process, the hides and skins are soaked in 200%-400% of water, by weight of skin or hide, two or three times for 10 minutes each time. In the first time, 0.1 preservative and 0.2% wetting agent are added to help in the removal of dung and dirt (Ramanujam et al., 2010; UNEP, 1996).

- Unhairing and Liming

This process is conducted in order to remove hair and epidermis, and to reduce the inter-fibrillary proteins. During this process, hides and skins are treated using 3% sodium sulfide, and 2% calcium hydroxide (hydrated lime) in 200% of water. Sodium sulfide facilitate the removal of keratin-based structures which are hair and epidermis, on the hand, hydrated lime acts as a buffer to maintain the high pH level required for softening the hide and facilitating the removal of the inter-fibrillary proteins. This process is repeated once more using 300%-400% water, lime and small quantities of soda ash or sodium hydroxide were added to obtain better softening of hides and skins (Ramanujam et al., 2010; UNEP, 1996).

- Deliming

During this process, the hides and skins are treated using a solution of 200% water and 1% ammonium chloride to remove the remaining alkalinity caused by lime. In addition, 2-3 % of degreasing agents are added to remove grease, and 1% bating enzyme are added to digest and remove the remaining inter-fibrillary proteins. Then, 200% water is used for washing (Ramanujam et al., 2010).

### 2.1.2 Tanning Stage

In this stage, the hides are treated using tanning agent, which is the trivalent chromium salts, in case of chrome tanning, to remove the intercellular water and stabilize the collagen fibers to increase its resistance to heat, hydrolysis and microbial degradation. This stage includes two processes: pickling and chrome tanning (Nazer et al., 2006).

- Pickling

This process is a pretreatment step that facilitates the tanning process. 10% sodium chloride, 1% sulfuric acid and 0.5% formic acid are added to 100% water to pickling solution for the delimed hides and skins and the pH range is maintained to be 2.8-3.2 for chrome tanning (Ramanujam et al., 2010).

- Chrome Tanning

After the pickled hides are released partially from the pickling liquor, they are tanned using 8% w/w of basic chromium sulfate. To increase the alkalinity of the content to pH of 3.8- 4.0, to fix the chromium, a solution of 1% sodium carbonate and 1% sodium formate dissolved in 50% water is used. Then, a solution of 0.1% preservative and 100% water is added. The tanning process takes 4 – 24 hours and the tanned hides are called wet blues. After that, the wet blues are dewatered, shaved and weighed. Based on the new weight of the wet blues, the amounts of water and chemicals used in the upcoming processes are identified (Ramanujam et al., 2010; Nazer et al., 2006).

### 2.1.3 Post-Tanning Stage

This stage is the final stage that prepare the tanned leather for fabrication. It includes re-tanning, neutralization, dyeing, fat liquoring and any other process needed for certain properties required in leather.

- Re-tanning

After washing the wet blues, they are re-tanned using a tanning solution consisting of 5% basic chromium sulfate and 150 % water. Also, in order to help in fixing the chromium, 1% sodium carbonate and 1 % sodium formate are used in the process (Ramanujam et al., 2010).

- Neutralization

The purpose of this stage is to remove the acidity and prepare the tanned leather for dyeing and fat liquoring. The wet blues are washed using 200% water and neutralized by adding 1% of sodium formate and 1% of sodium bicarbonate. The final pH of the tanned leather is 4.8 – 5.3 (Ramanujam et al., 2010).

- Dyeing and fat liquoring

These two processes are usually conducted in the same container. After washing the tanned leather with 200% water, 200% hot water at temperature of 60 °C with 4% required dye is added to color the leather. Then, 12% of animal fat liquor is added to re-establish the fat content and give the leather the final appearance (Ramanujam et al., 2010).

## **2.2 Tanning Wastewater Characteristics**

According to the previous explanation of tanning processes, tanning industry is considered as highly environmentally polluting industry due to the large amounts of chemicals residues, large amounts of organic wastes and waste effluents are produced during these different processes. The total volume of wastewater produced from tanning processes for 1 ton is ranged from 30 to 56 m<sup>3</sup> (Ayaliw et al., 2014; El-Khateeb et al., 2017). However, the characteristics of the tanning wastewater and type of contaminants differ according to the stage of the industry produced from as shown in Figure 2.1 (Dixit et al., 2015; Sabumon, 2017).

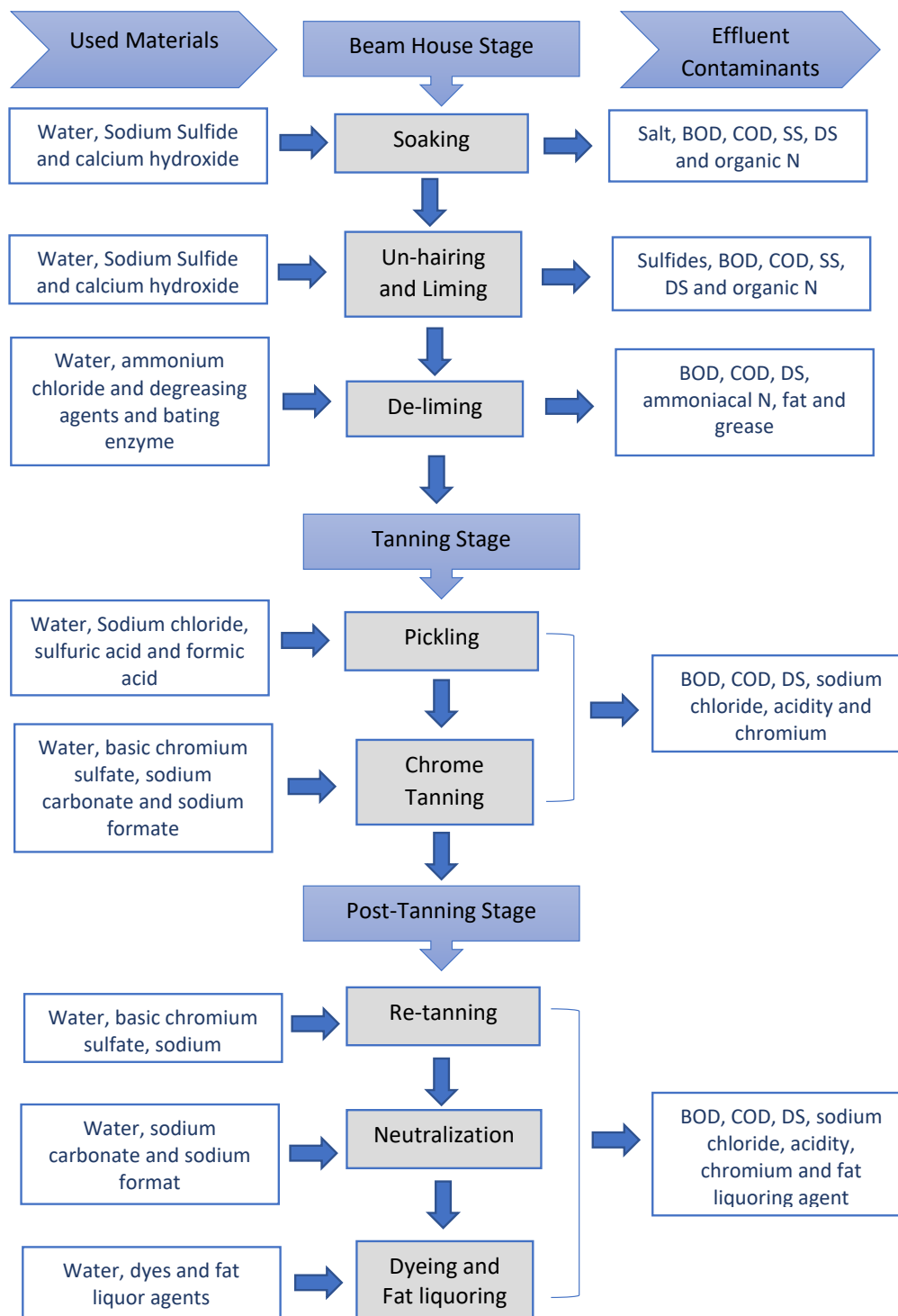


Figure 2.1: Inputs and Outputs of Tanning Processes



The effluents discharged from soaking process ranged from 7 to 9 m<sup>3</sup>/ton raw hides. The main contaminants in the effluents are salt residues due to hides preservation, dirt and protein matters. For the unhairing and liming process, the discharged effluents ranged from 9 to 15 m<sup>3</sup>/ton raw hides. These effluents are considered as the most polluted effluents discharged during tanning processes as they contain large amounts of sulfides, lime, decomposed hair keratin and non-collagen proteins as shown in Table 2–1 (Ludvik, 2000). Sulfides in liming effluents are considered as one of the most dangerous pollutants discharged from tanning processes as they react with the hydrogen ions in the acidic media resulted from mixing the liming effluents with other acidic effluents discharged from tanning processes to produce hydrogen sulfide gas which is a very toxic and corrosive gas (Nazer et al., 2006). On the other hand, the effluents discharged from deliming process ranged from 7 to 11 m<sup>3</sup>/ton raw hides and they contain calcium salts, ammonia, sulfide residues, degraded collagen protein, decomposed hair keratin and residual enzymatic agents (Ludvik, 2000). Generally, as shown in Figure 2.2, beam house stage effluents represent 62.5% of the total tannery effluents. In addition, according to the pollutant loads summarized in Table 2–1 beam house stage processes discharge around 76% of the total BOD and COD, 85% of the total suspended solids and 65% of total chloride amounts in tanneries effluents.

Table 2–1: Pollution Loads for Each of Tanning Processes (Ludvik, 2000)

Process	Pollution Loads per ton of hides (Kg/t)								
	BOD	COD	SS	Cr <sup>3+</sup>	S <sup>2-</sup>	Ammoniacal N	Organic N	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2+</sup>
Soaking	7 - 11	22 - 33	11 - 17	-	-	0.1 - 0.2	1 - 2	85 - 113	1 - 2
Liming	28 - 45	79 - 122	53 - 97	-	3.9 - 8.7	0.4 - 0.5	6 - 8	5 - 15	1 - 2
Deliming	5 - 9	13 - 20	8 - 12	-	0.1 - 0.3	2.6 - 3.9	3 - 5	2 - 4	10 - 26
Tanning	2 - 4	7 - 11	5 - 10	2 - 5	-	0.6 - 0.9	0.6 - 0.9	40 - 60	30 - 55
Post-tanning	8 - 15	24 - 40	6 - 11	1 - 2	-	0.3 - 0.5	1 - 2	5 - 10	10 - 25
Finishing	0 - 2	0 - 5	0 - 2	-	-	-	-	-	-
Total	50 - 86	145 - 231	83 - 149	3 - 7	4 - 9	4 - 6	12 - 18	137 - 202	52 - 110

## Effluent Percentages of Different Tanning Stages

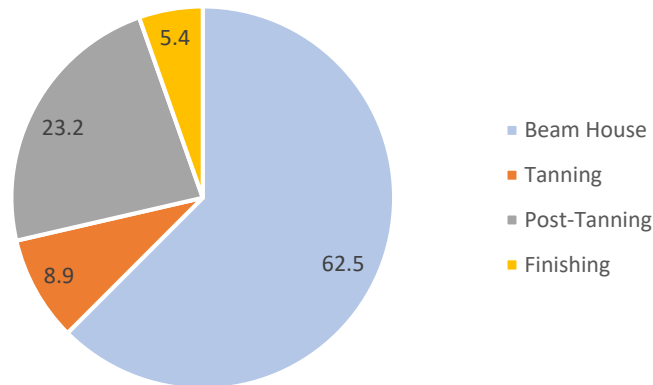


Figure 2.2: Effluents Percentages for Tanning Stages

The effluents discharged from tanning processes, which are pickling and chrome tanning, are acidic effluents and their amounts ranged from 3 to 5 m<sup>3</sup>/ton raw hides in which the main contaminants are unreacted chromium, chlorides and sulfates. It can be observed, from the data in Table 2–1, that around 71% of the total amount of chromium contaminants are discharged from the chrome tanning process. Also, the post-tanning processes discharged acidic effluents ranged from 7 to 13 m<sup>3</sup>/ton raw hides and the main contaminants in the effluents are chromium, dyes residues, fat liquoring agents and other organic matters. 50% of the chromium contaminants, discharged from post-tanning stage, are produced from the re-tanning process, 20% from dyeing process and 30% from fat liquoring process (Ludvik, 2000).

### 2.3 Treatment Methods

As indicated in the previous section, tanneries effluents are heavy polluted effluents which represent a serious environmental and health problem due to the high amounts of chemical and biological contaminants discharged from different tanning processes. The characteristics of the effluents varies according to the process discharged from, so it is preferred to pre-treat these effluents separately in order to minimize the cost of treatment and avoid hazardous risks like forming toxic gases like hydrogen sulfide gas (Nazer et al., 2006; UNIDO, 2011). In the following sections, the conventional and advanced treatment methods of tanneries effluents will be discussed.

### 2.3.1 Conventional Tanneries Wastewater Treatment

Conventional tanneries wastewater treatment method is the applied method of treatment in many countries to guarantee the quality of tanneries effluents disposed in the environment. The conventional treatment method consists of four stages comprising primary treatment, secondary treatment, tertiary treatment and sludge disposal.

- Primary Treatment

This stage aims to remove coarse matters, chromium III, sulfides and most of suspended solids through four steps of screening, equalization and sulfide oxidation, chemical treatment and settling as shown in Figure 2.3. During screening step, the effluents go through bar screens to remove coarse matters and through fine screens to reduce fine suspended solids. In the equalization and sulfide oxidation step, mixing-cum-aeration devices are used to keep the effluent homogeneous and avoid suspended solid settling; in addition, sulfides are eliminated by catalytic oxidation (UNIDO, 2011). The chemical treatment step is conducted through coagulation and flocculation processes. During this step, coagulants, like alum, iron sulfate, iron chloride or lime, are used to destabilize colloids by charging them with positive charge to facilitate flocs formation during flocculation process. During this step, chromium contaminates in the effluents precipitate as chromium hydroxide and are removed with the other suspended solids during the settling step (UNIDO, 2011; Reynolds & Richard, 1996).

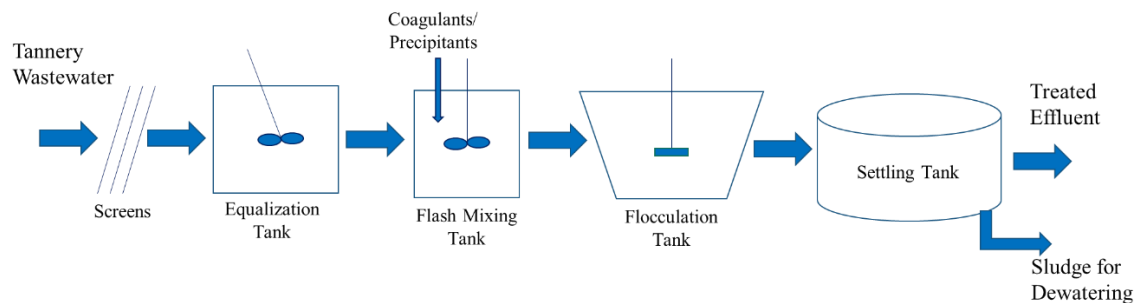
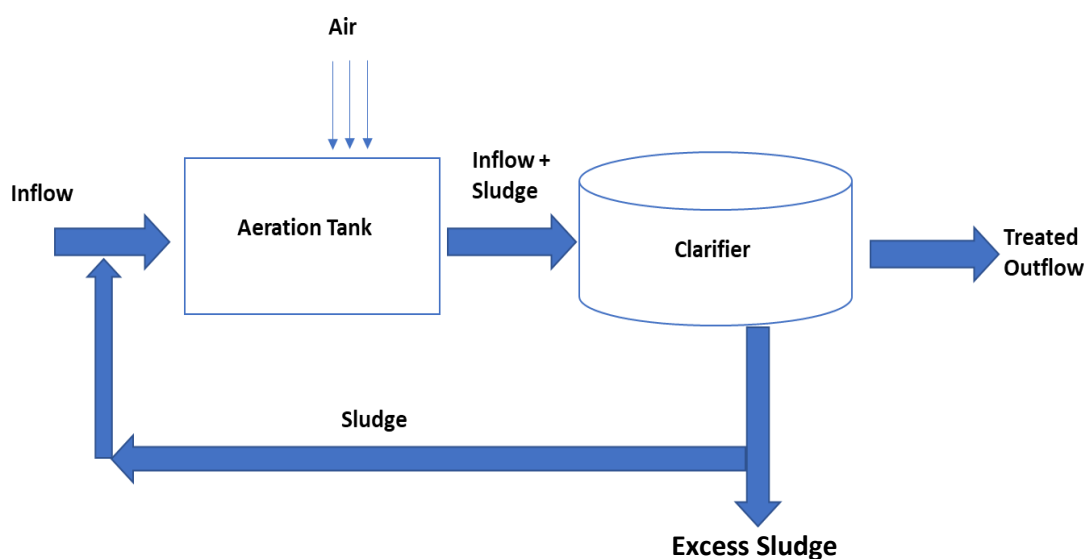


Figure 2.3: Schematic Diagram for Primary Treatment Stage

- Secondary Treatment

Secondary treatment is basically a biological treatment conducted to remove organic matters causing high COD, BOD and any other substances remaining from the primary treatment. The most common biological treatment used in tanneries wastewater treatment is the activated sludge with extended aeration method. This method is an aerobic biological method that depends on using micro-organisms to digest organic matters in presence of oxygen in aeration tank then the effluents are kept for settling in the clarifier as shown in Figure 2.4 ( UNIDO, 2011).



*Figure 2.4: Schematic Diagram for Secondary Treatment Stage*

- Tertiary Treatment

Tertiary treatment is an optional stage conducted in case the quality of the treated wastewater, produced from primary and secondary treatment, doesn't satisfy the required specifications. During this stage,  $H_2O_2$  oxidation and ozonation processes are conducted for further treatment to eliminate any compounds that the micro-organism cannot digest.

### 2.3.2 Other Treatment Methods for Chromium Removal

Chromium removal is one of the important targets of tanneries wastewater treatment processes due to its hazardous effects on human health and the environment. However, the conventional treatment method explained in the previous section usually

doesn't show effective performance in chromium removal. As a result, other advanced treatment methods are studied recently to be used in chromium removal from tanneries wastewater. Some of these methods will be discussed in the following sections (El-Khateeb et al., 2017).

#### *2.3.2.1 Ion Exchange*

Ion exchange is a water and wastewater treatment method which is based on exchanging the ions of the dissolved contaminant with the ions with the same charge that belongs to other substance called “resin” (New Hampshire Department of Environmental Services, 2009). Ion exchange resin is a polymer or solid substance which has the ability to sorb the ions of the contaminant, dissolved in the solution go through it, and replace them with its ions that have the same charge (Patel, 2016; Reynolds & Richard, 1996). Ion exchange treatment is studied for chromium removal for both states of oxidation, Cr III and Cr VI, and it showed good removal efficiency. For the removal Cr VI, various resins were used in the removal of Cr VI and the removal efficiency reached 99 % without changing the pH of the solution (Kumar et al., 2008; Shi et al., 2009). In addition, ion exchange was studied for Cr (III) removal from tannery wastewater and the removal efficiency also reached 99% using strongly acidic cation resins (Cetin et al., 2013; Meshram et al., 2012). There are many advantages for ion exchange treatment method that motivated using it in chromium removal including low running cost, low required energy and the low cost of regenerate chemicals for the resins. However, resins in ion exchange method tend to adsorb and accumulate organic matter which affects the sorption capacity of the resin and enhance bacterial growth. Also, chlorine residues in wastewater cause serious damage for resins and reduce their life time (Patel, 2016).

#### *2.3.2.2 Adsorption*

According to Reynolds & Richard, 1996, adsorption process is a treatment process that depends on collecting the contaminants onto the surface of the adsorbent particles. There are two types of adsorption according to the bonding type between the adsorbent and adsorbate; the first type is physical adsorption and the second type is chemical adsorption. Physical adsorption is widely used in environmental engineering and the common adsorbent used in industrial wastewater treatment is activated carbon (Grassi et al., 2012;

Reynolds & Richard, 1996). Adsorption treatment using activated carbon was used in chromium removal from tanneries wastewater and the removal efficiency reached 56% using commercial activated carbon, 78% using activated carbon derived from tannery wastes and 86-98% using activated carbon derived from sugar industrial wastes (Fahim et al., 2006; Itodo et al., 2018; Louarrat, 2018). Despite the effectiveness of activated carbon in chromium removal, the high cost and energy consumption of activated carbon preparation process are considered as significant disadvantages of this treatment method (Grassi et al., 2012). As a result, several researches were conducted to study the efficiency of using other low-cost materials as adsorbents for the removal of heavy metals, like chromium, from industrial wastewater. Organic and inorganic wastes and byproducts were used as low-cost adsorbents and they showed good treatment performance as will be discussed in the upcoming sections. However, the removal efficiency of these adsorbents varies depending on the characteristics of the material; in addition, some of the organic wastes, like rice straw, rice husk, wheat straw and others, need chemical modification in order to increase their removal efficiency which increase the treatment cost (Grassi et al., 2012). In addition, there are many factors affecting adsorption process like initial ion concentration, adsorbent dosage, temperature, pH value, contacting time, ionic strength and the interaction between the adsorbent and adsorbate; these factors put certain limitations on the application of adsorption treatment (Sadegh & Ali, 2018)

#### *2.3.2.3 Membrane Separation*

Membrane separation is one of the advanced treatment methods used in separating heavy metals ions from industrial wastewater. Membrane separation method is based on separating contaminants from wastewater using selectively permeable membrane and under certain driving force to cause mass transfer (Reynolds & Richard, 1996). There are three types of membrane separation including dialysis, electrodialysis and pressure-driven membrane separation. The driving force required for separation varies according to the type of membrane separation; it is difference in concentration for dialysis, electric potential for electrodialysis and applied pressure for pressure-driven membrane separation. Pressure-driven membrane separation is the common type used in industrial wastewater treatment and it is classified, according to pore size of the membrane and the applied

pressure, into four types include microfiltration, ultrafiltration, nanofiltration and reverse osmosis as shown in Table 2–2 (Kocurek et al., 2015).

*Table 2–2: Pressure-driven Membrane Separation Processes (Kocurek et al., 2015)*

<b>Membrane Separation Process</b>	<b>Particle Size</b>	<b>Operating Pressure</b>
<b>Microfiltration</b>	>0.1 $\mu\text{m}$	<500 kPa
<b>Ultrafiltration</b>	10 – 100 nm	1000 kPa
<b>Nanofiltration</b>	1 – 10 nm	4 MPa
<b>Reverse Osmosis</b>	0.1 – 1 nm	10 MPa

Microfiltration and ultrafiltration are suitable for the removal of suspended solids, colloids, bacteria and viruses and high-molecular substances as their separation mechanism is based on sieve effect, so they are usually used in pre-treatment stage. On the other hand, nanofiltration and reverse osmosis are suitable for separating monovalent and polyvalent ions as their separation mechanism is based on diffusion; however, the reverse osmosis efficiency is more than nanofiltration efficiency (Kocurek et al., 2015). Reverse osmosis separation is the suitable type used in chromium removal from tanneries wastewater and the removal efficiency of this method can reach 100% for low chromium concentration solutions. However, this high efficiency decreases in case of high chromium concentration or in case of presence of other contaminants that can clog the pores of the membrane and reduce the separation efficiency. As a result, reverse osmosis is used as a second step after conventional pretreatment stage, which include screening, coagulation and sedimentation, which increases the treatment cost (Kocurek et al., 2015; Mohammed & Sahu, 2019; Tripathi & Dwivedi, 2012).

## **2.4 Chemical Precipitation Treatment Method**

Chemical precipitation is a common industrial wastewater treatment method which is based on converting soluble metallic ions or other anions to insoluble precipitate form that can be easily removed by sedimentation or filtration (Wang et al., 2005). Chemical precipitation is commonly used in the removal of heavy metals, phosphorous and hardness

using common precipitants like calcium hydroxide, sodium hydroxide, magnesium oxide and calcium carbonate. The efficiency of chemical precipitation treatment method is affected by several factors include the type of precipitation agent, pH, velocity of precipitation, sludge volume, time of mixing and complexing agents (Abdulla & Ahmed, 2010; Kocaoba & Akcin, 2002).

Chemical precipitation is conducted through the conventional treatment process in which the precipitant is added in the flash mixing tank to be mixed with wastewater then transferred to the flocculation tank for gentle mixing in order to complete the precipitation reaction and facilitate precipitate flocs formation. Finally, the treated wastewater is separated through sedimentation process and the precipitated sludge goes through dewatering process.

#### 2.4.1 Chemical Precipitation Types

Chemical precipitation treatment is classified, according to the mechanism and type of precipitate, into several types; however, the common types used for heavy metal removal are hydroxide, sulfide and carbonate precipitation.

##### 2.4.1.1 Hydroxide Precipitation

This type of chemical precipitation is the common type used in the removal of heavy metals. The mechanism of this type is based on using alkaline agents to raise the pH value of wastewater to the pH value in which the solubility of the metal is in the minimum level, so the dissolved metal is chemically precipitated in form of hydroxides and the form of this reaction can be expressed as following (L. Wang et al., 2005):



Where:

$M^{n+}$ : Metal ion

$(OH)^{-}$ : Hydroxide ion

$M(OH)_n$ : Metal Hydroxide



The pH value in which the metal reaches its minimum solubility varies according to the type of the metal and it can be identified from the solubility curves of the metals shown in Figure 2.5.

The common alkaline agents used to raise the pH in industrial wastewater treatment include calcium oxide (lime), calcium hydroxide (Hydrated Lime), sodium hydroxide and magnesium oxide (Abdulla & Ahmed, 2010). Although lime is the common precipitant used in hydroxide precipitation due to its high treatment efficiency and low cost compared to the other precipitants, using lime for treating wastewater includes sulfate ions resulting in forming calcium sulfate (gypsum) which increases sludge production and causes scaling problem in pipelines (L. Wang et al., 2005).

Hydroxide precipitation is conducted in combination with coagulation and flocculation processes through the conventional treatment method which resulted in producing high quality treated effluents (EPA, 2000; L. Wang et al., 2005). In addition, the main advantages of hydroxide precipitation are the availability of low-cost precipitants and the low maintenance required for the systems and units used in the precipitation process (EPA, 2000).

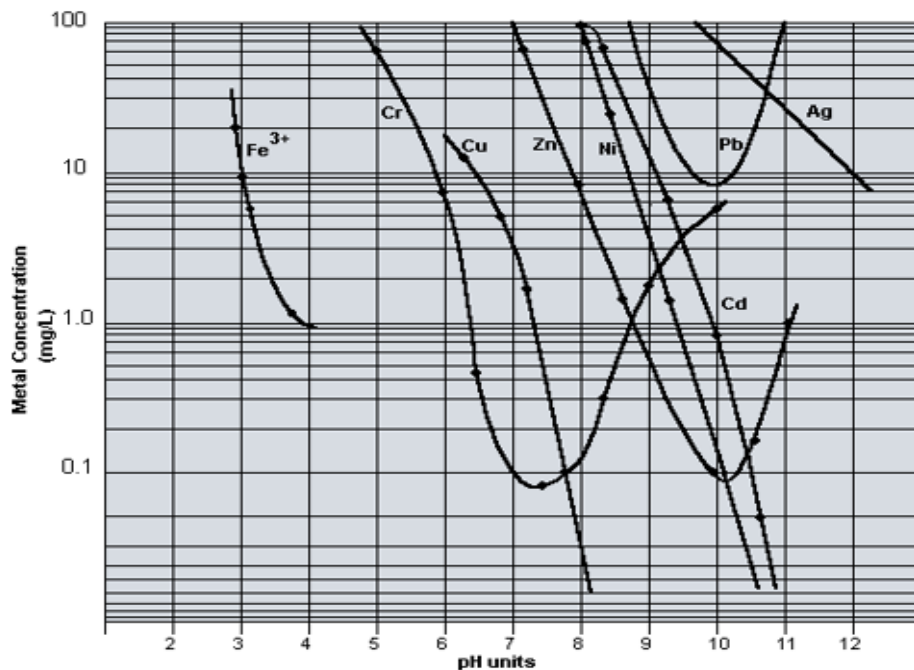


Figure 2.5: Metal Hydroxides Solubility Curves (Hoffland Environmental Inc., 2017)

#### *2.4.1.2 Sulfide Precipitation*

This type of chemical precipitation is also used in heavy metals removal from industrial wastewater and its mechanism is close to the hydroxide precipitation mechanism. The mechanism of this type is based on using soluble and insoluble sulfides to precipitate heavy metal ions as metal sulfides which have low solubility in all pH ranges. The common sulfides used in this type include sodium sulfide, sodium bisulfide and ferrous sulfide. However, this type of chemical precipitation requires pretreatment and post treatment due to the toxicity of the sulfides released in the treated wastewater (Wang et al., 2005).

#### *2.4.1.3 Carbonate Precipitation*

The mechanism of this type of chemical precipitation is based on precipitating metal ions in form of metal carbonates, which is insoluble in all pH ranges, by using carbonate reagents like calcium carbonate or by converting hydroxides into carbonates using carbon dioxide. This process is commonly used in water softening (Wang et al., 2005).

### *2.4.2 Chemical Precipitation for Chromium Removal from Tannery Wastewater*

As discussed in the previous section, hydroxide precipitation is the classical treatment method for heavy metals removal from industrial wastewater (L. Wang et al., 2005). As a result, various researches were conducted in order to compare between the removal efficiencies of different precipitants and to improve their treatment performance. In his research work, Minas et al., 2017 conducted a comparison study between sodium hydroxide (NaOH), calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and magnesium oxide (MgO) based on their removal efficiency of trivalent chromium and their treatment performance. The results showed that there is no significant difference in the removal efficiency of these precipitants as the removal efficiency of all of them exceeds 99% at the optimum pH value. However, it was observed that the highest settling rate and lowest sludge volume were obtained by using MgO as precipitant. In addition, although the optimum pH for minimum chromium solubility obtained from the solubility graph in fig. 2.5 was 7.5, the optimum pH for chromium precipitation using MgO and  $\text{Ca}(\text{OH})_2$  ranged from 9.8 to 10.3. According to Minas et al., 2017, these results indicated that MgO and  $\text{Ca}(\text{OH})_2$  are acting as coagulants during precipitation and enhance the removal efficiency. Esmaeili et al., 2005 also had the

same results that recommended using MgO for chromium precipitation from tanneries wastewater and indicated that the optimum pH for chromium precipitation ranged from 8 to 9. However, the main problem of these results is that MgO is relatively expensive compared to (NaOH) and (Ca (OH)<sub>2</sub>). On the other hand, Guo et al., 2006 proposed a solution to this problem by using a mixture of calcium oxide (CaO) and magnesium oxide (MgO) with optimum ratio of 4:1, respectively, which give the same efficiency but with lower cost. Also, Ramakrishnaiah & Prathima, 2012 used a combination of CaO and NaOH for hexavalent chromium removal which decreased the sludge volume and increased the settling rate. Based on these studies and results, hydroxide precipitation is a promising treatment method that can be developed to be more effective and economical.

## **2.5 Solid Wastes for Low-Cost Treatment**

Due to the low treatment efficiency of conventional treatment methods and the high cost of advanced treatment methods, many researches were conducted in order to develop low-cost effective treatment techniques for industrial wastewater (El-Khateeb et al., 2017). As a result, various studies were conducted to investigate the efficiency of using organic and inorganic wastes and by-products as adsorbents or precipitants for industrial wastewater treatment. In addition, some organic waste materials ashes, especially agricultural wastes, are considered as rich source of activated carbon that can be used in the adsorption process instead of commercial high cost activated carbon. The treatment efficiency of some of these wastes and by-products will be discussed in the following sections.

### **2.5.1 Rice Straw**

According to FAO, Egypt is the largest rice producer in Africa as the Egyptian production of rice represents 22% of the rice production in Africa. However, Egypt produced 5.1 million of rice straw in which 3.1 million are burning in the open field annually (Abdelhady et al., 2014). This type of disposal of rice straw represents a seasonal problem as it causes the annual black cloud which is a serious air pollution problem (Amer et al., 2017). However, in case of industrial wastewater treatment, rice straw is indicated as an important adsorbent used in the removal of heavy metals (Mary Lissy & Madhu, 2010; Rocha, et al., 2009). According to Rocha et al., 2009, the efficiency of using rice straw in

the removal of Copper (Cu (II)), Zinc (Zn (II)), Cadmium (Cd (II)) and Mercury (Hg (II)) has been investigated and the results revealed that rice straw showed a good adsorption capacity. The optimum adsorption capacity has been reached at pH 5.0 to be 0.128, 0.132, 0.133 and 0.11mmol/g for Cu (II), Zn (II), Cd (II) and Hg (II), respectively. In addition, the study revealed that rice straw biosorbent can be regenerated using hydraulic acid maintaining the uptake capacity for fifteen cycles. Raw rice straw was also used in lead removal and its maximum removal efficiency recorded 94% with maximum adsorption capacity of 42.55 mg/g (Amer et al., 2017). On the other hand, Mary Lissy & Madhu, 2010 indicated that treating powdered rice straw using sodium hydroxide (NaOH) increased the removal of Nickel (Ni) from 60 to 80%. In case of chromium removal, rice straw recorded a high adsorption capacity of 3.15 mg/g in the removal of hexavalent chromium (Cr VI).

### 2.5.2 Rice Husk

Rice husk is the outer cover of the grains of rice and it is considered as waste material generated during rice milling process. Organic matter like lignin, cellulose, hemicellulose and sugar represents 70 -85% of the dry weight of rice husk (Malik et al., 2016). According to several studies, rice husk is a good biosorbent that can be used for heavy metals removal from water and wastewater. Rice husk recorded adsorption capacity of 416.787 µg/g in arsenic (V) removal from drinking water (Asif & Chen, 2017), and 100 % removal efficiency of arsenic (III) and arsenic (V) from aqueous solution with initial concentration of 100 µg/l (Mohan & Pittman, 2007). Also, Sobhanardakani et al., 2013 used rice husk for chromium (III) and copper (II) removal from synthetic wastewater and the sorption capacity reached 22.5 mg/g for chromium (III) removal and 30 mg/g for copper (II) removal. On the other hand, chemical modification increased the removal efficiency of cadmium (II) of rice husk from 75% to 97% (Kumar & Bandyopadhyay, 2006). Rice husk could be also used to produce activated rice husk carbon which recorded 93.28% removal efficiency of chromium (VI).

### 2.5.3 Sugarcane Bagasse

As sugar industry is one of the oldest industries in Egypt, sugarcane bagasse is one of the agricultural wastes available in abundance in Egypt. Like rice straw and rice husk, Sugarcane bagasse contains cellulose, lignin, silica and other elements that induce

adsorption capacity (Homagai et al., 2010). Untreated sugarcane bagasse recorded sorption capacity of 2 mg/g for nickel removal (Aloma et al., 2002). However, according to Homagai et al., 2010, the adsorption capacity for nickel significantly increased after treating sugarcane bagasse with sulfuric acid and sodium hydroxide to be 2.52 mol/kg (147.9 mg/g) (Homagai et al., 2010). In addition, the adsorption capacity for lead removal of sugarcane bagasse treated with sulfuric acid and sodium hydroxide recorded 1.58 mol/kg (327.38 mg/g) which is higher than the adsorption capacity of sugarcane bagasse treated by sulfuric acid only for lead removal which was 7.297 mg/g (Homagai et al., 2010; Martín-Lara et al., 2010). Also, treated sugarcane bagasse recorded adsorption capacity of 5.122 mg/g which is higher than the adsorption capacity recorded for untreated sugarcane bagasse which was 4.018 (Mahmood-ul-Hassan et al., 2015).

#### 2.5.4 Sawdust

Sawdust is one of the agricultural wastes which contain lignin, cellulose, and hemicellulose, with polyphenolic groups which play an important role in binding the heavy metal ions with the biosorbent (Ouafi et al., 2017). Ahmad et al., 2009 investigated the efficiency of treated sawdust in copper (II) and lead (II) removal and the results revealed that the removal efficiency recorded 100% for copper (II) removal at pH 6.6 and 94.61% for lead (II) removal at pH 7.0. In addition, raw sawdust was used as an adsorbent for lead (II), cadmium (II) and Nickel (II) removal and the maximum adsorption capacities were 6.68 mg/g for lead (II) at 45°C, 4.9 mg/g for cadmium (II) and 2.79 mg/g for Nickel (II) at 60°C (Yasemin & Zeki, 2006). Also, Gupta & Babu, 2009 studied the performance of sawdust in Cr (VI) removal and stated that sawdust is better adsorbent for the removal of Cr (VI) compared to many other low cost and commercially available adsorbents. The study concluded that the maximum adsorption capacity was 41.52 mg/g. In addition, sawdust could be regenerated using acid and base treatment and the adsorption efficiency of the regenerated sawdust was found to be more than 95% of fresh sawdust for the removal of Cr (VI).

#### 2.5.5 Cement bypass kiln dust

Cement bypass kiln dust is the alkaline fine particulate material generated during calcination process which is rejected from the kiln system in order to reduce the alkalinity of the clinker during the manufacture of Portland cement (Ali et al., 2011; Mackie & Walsh, 2012). It consists of a mixture of chemical compounds in which calcium oxide (CaO) is the major constitute and the other constitutes include silicon dioxide (SiO<sub>2</sub>), Aluminum Oxide (Al<sub>2</sub>O<sub>3</sub>), ferric Oxide (Fe<sub>2</sub>O<sub>3</sub>), potassium oxide (K<sub>2</sub>O), sodium oxide (Na<sub>2</sub>O), chloride ions (Cl<sup>-</sup>) and other compounds (Ali et al., 2011; Zaki et al., 2007). Egypt Produces around 1 million tons of cement bypass kiln dust annually which is very alkaline and cannot be reused in the cement manufacturing (Mostafa et al., 2005). Due to its alkalinity nature, cement kiln dust could be used to remove heavy metals from industrial wastewater. Zaki et al., 2007 used cement bypass kiln dust leachate, which is a very alkaline solution (pH > 12), to completely precipitate copper (II), Nickel (II), and zinc (II) from synthetic solutions at pH values of 5.5, 7 and 7.3, respectively. In addition, cement bypass kiln dust was used in tanneries wastewater treatment and the results showed significant reduction in the concentrations of chromium III, TSS and COD by 31, 92.1 and 91.3 %, respectively (Mostafa et al., 2005).

#### 2.5.6 Marble Powder

Egypt is one of the countries which produce marble in large quantities, however, during marble processing, marble powder or marble dust is generated as by-product (Ghazy & Gad, 2008). Due to the availability and low cost of marble powder, many studies investigated its efficiency in heavy metals removal. Ghazy & Gad, 2008 indicated that using marble powder for zinc (II) removal resulted in approximately 100% removal of zinc (II). In addition, the efficiency of using marble powder in copper (II) removal from drinking water was investigated and the results indicated that the removal of Cu<sup>2+</sup> ions occurred mainly due to adsorption at pH < 6.0; however, at pH > 6.0, complete removal occurred due to both the concurrent precipitation of copper hydroxide (Cu (OH)<sub>2</sub>(s)) and adsorption (Ghazy et al., 2003). On the other hand, Elabbas et al., 2016 conducted batch adsorption tests in order to study the efficiency of using marble powder in chromium (III) removal from tanneries wastewater. The results indicated that the maximum adsorption

capacity was 262 mg/g at pH 5.0 and dose of 12 g/l of marble powder for initial concentration of chromium up to 3.21 g/l.

## 2.6 Chromium Recovery

Around 30 to 40 % of the basic chromium sulfate used in tanning process is discharged in the tanneries wastewater which represents an environmental and economic problem due to the serious environmental problems caused by chromium contamination and the increase in the cost of basic chromium sulfate (Wang, 2019). Since 1978, several studies were conducted to investigate the efficiency of recovering basic chromium sulfate from chromium sludge precipitate. The basic theory of chromium recovery is precipitating chromium from tanning wastewater as chromium hydroxide  $\text{Cr}(\text{OH})_3$ , using an alkali like magnesium oxide ( $\text{MgO}$ ), and dissolving the precipitated sludge using sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in order to form concentrated solution of chromium sulfate ( $\text{Cr}_2(\text{SO}_4)$ ) (Pansward et al., 2001). Minas et al., 2017 used 3 ml of concentrated  $\text{H}_2\text{SO}_4$  to recover chromium from  $\text{Cr}(\text{OH})_3$  sludge precipitated using  $\text{MgO}$  at pH of 2.8 and the results showed recovery efficiency of 30% of precipitated chromium. On the other hand, using microwave irradiation to enhance the dissolution of chromium sludge in concentrated  $\text{H}_2\text{SO}_4$  increased the recovery efficiency from 60 to 80 % (Guo et al., 2006). Moreover,  $\text{H}_2\text{SO}_4$  solution with concentration of 1.0 N was used to recover chromium adsorbed by activated carbon and the recovery efficiency reached 98% (Hintermeyer & Tavani, 2017).

## **Chapter 3: Materials and Methods**

### **3.1 General**

This study was conducted to investigate the performance of different types of solid wastes in the recovery of trivalent chromium. In order to reach this target, the study was conducted in five different phases as will be described later in section 3.2. The first 3 phases were conducted to investigate the optimum conditions for chromium removal from synthetic aqueous solution using solid waste materials, while the other two phases were conducted to investigate the efficiency of the treatment method on real samples of tanneries wastewater and the efficiency of trivalent chromium recovery. All the experiments in the different phases and most of sample analyses were conducted in the Environmental Engineering Laboratory at the American University in Cairo.

### **3.2 Phases of Study**

This study was conducted in 5 phases: phase I, phase II, phase III, phase IV and phase V. In phase I, two groups of waste materials were tested for the removal of trivalent chromium from aqueous solution. The first group included organic solid wastes namely rice husk (RH), rice straw (RS), sugarcane bagasse (SB) and sawdust (SD), while the second group included inorganic solid wastes namely cement bypass kiln dust (CKD) and marble powder (MP). In phase II, the waste materials with higher Cr III removal efficiency, obtained from phase I, were selected for further investigation. In phase II, jar tests were conducted in order to identify the optimum mixing conditions and the energy required in the treatment process, due to mixing, for the selected materials. In phase III, one type of waste material, based on the removal efficiency of Cr III and energy consumption in phase II, was selected for further investigation on its performance, operating conditions and possible mechanisms for the removal of trivalent chromium. In phase IV, real wastewater was collected from a tannery in Egypt and it was tested for Cr III removal using the selected waste material under the mixing and operating conditions obtained in phases II and III. Finally, in phase V, the characteristics of the precipitated sludge generated due to Cr III removal were studied, and complete analysis was conducted. In addition, the optimum conditions for the recovery of chromium III from the precipitated sludge were studied using



sulfuric acid ( $\text{H}_2\text{SO}_4$ ). In the following sections, more details will be provided on the materials and methods used in each phase.

### **3.3 Phase I: Solid wastes Comparative Study**

In this phase, batch experiments were conducted to investigate the possibility of Cr III removal using waste materials that can be categorized under two groups organic and inorganic wastes.

#### **3.3.1 Preparation of Solid Waste Materials for Phase I Experiments**

As mentioned before, the solid waste materials investigated in this phase can be categorized under two main groups, organic and inorganic waste materials. Organic waste materials include solid wastes from agricultural and industrial activities such as rice straw (RS), rice husk (RH), sugarcane bagasse (SB) and sawdust (SD). Inorganic waste materials include solid wastes from industrial activities such as cement bypass kiln dust (CKD) and marble powder (MP). In the following two sections, more details will be given about the preparation of waste materials in order to be used in the removal of Cr III.

##### *3.3.1.1 Preparation of Organic Waste Materials*

The Organic waste materials were prepared before conducting the experiments by washing them for 3 times using tap water. Then, they were rinsed with distilled water in order to remove any dust or soil residues that might be attached to them. After washing, the waste materials were dried in the sun for 24 hours, then in the oven at  $80^\circ\text{C}$  for seven hours or till reaching complete dryness. After oven drying, waste materials were ground using mechanical grinder then sieved using mechanical sieving system on a 100/200 sieve to obtain particle size of 150 to  $75\ \mu\text{m}$ ; this size range is within the range reported in different studies for these materials when used for heavy metals removal from aqueous solutions (Amer, 2015, and Gurel & Gel 2009, Mahmood-ul-Hassan et al, 2015 and Abdulla & Ahmed, 2010 and Rocha, 2009).

##### *3.3.1.2 Preparation of Inorganic Waste Materials*

The cement bypass kiln dust (CKD) was prepared by drying in the oven for 5 hours at  $100^\circ\text{C}$ . The drying process was important to remove any moisture could be included due to inappropriate storage. After drying, it was left to cool then sieved using sieve no.

140 to obtain the size of 106  $\mu\text{m}$  in order to remove impurities. The marble powder was ground using mechanical grinder, then oven dried at 100 C° for 5 hours like CKD. After cooling, the sample was sieved with sieve no. 140 to obtain a more uniform particle size of 106  $\mu\text{m}$ .

### 3.3.2 Preparation of Synthetic Solution for Phase I Experiments

In this phase, synthetic solution, containing Cr III at concentration of 1000 mg/l, was used in all experiments of this phase. In order to prepare the synthetic solution, 3.473 g of hydrate chromium sulfate ( $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ ) was dissolved in 500 ml of distilled water, then the solution was made up to 1000 ml using distilled water. The pH of the solution was then adjusted to a value of 3.0, to simulate the pH of real tannery's wastewater (Abdulla & Ahmed, 2010; Abbas et al., 2005 ), using 4M NaOH solution and 4M  $\text{HNO}_3$  solution.

### 3.3.3 Experimental Set up of Phase I Experiments

Seven high density polyethylene bottles, each with capacity of 125 ml, were used in the experiments of this phase as shown in Figure 3.1. Each bottle was filled with 50 ml of synthetic trivalent chromium solution with concentration of 1000 mg/l. Then, 1g of each type of the waste materials added to the 50 ml solution in each bottle. The bottles were mixed well then placed on a mechanical orbital shaker, as shown in Figure 3.2, at speed of 200 RPM for 60 min. After mixing and shaking of the reactors, liquid samples were filtered using cellulose acetate filter paper 0.45  $\mu\text{m}$  and the filtrates were collected for the analysis of trivalent chromium.



Figure 3.1:Labeled High Density Polyethylene Bottles



*Figure 3.2: HDP Bottles on the mechanical orbital*

### **3.4 Phase II: Effect of Mixing Conditions on the Removal of Cr III**

The purpose of phase II was to study the effect of mixing conditions on the removal of Cr III using the waste materials of the highest removal efficiency obtained from phase I. As will be discussed later in the results and discussion chapter, the inorganic waste material can remove Cr III at higher efficiencies compared to the organic waste materials. Therefore, the inorganic waste materials group were selected to be used in conducting the experiments of this phase. The mixing conditions can significantly affect the removal of metals from aqueous solution (Abdulla & Ahmed, 2010; Kocaoba & Akcin, 2002). Two main parameters control the mixing process; the first one is the flash mixing speed ( $G_{fm}$ ) and the second is Camp No. ( $G_{gmt}$ ). Camp No. represents the multiplication of flocculation mixing speed ( $G_{fm}$ ) and flocculation time ( $t$ ) as shown in Figure 3.3.

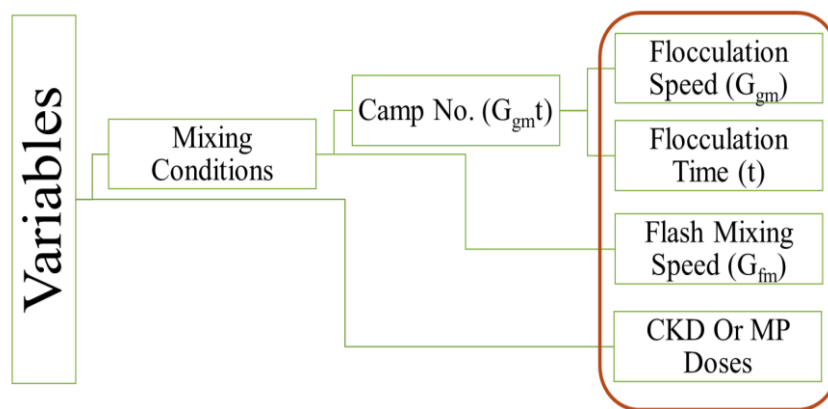


Figure 3.3: Experimental Variables in Phase II

#### 3.4.1 Preparation of Synthetic Solution for Phase II Experiments

In this phase, synthetic solution with Cr III initial concentration of 1000 mg/l was used to study the effect of mixing conditions on the removal of Cr III using cement bypass kiln dust (CKD) or marble powder (MP). For each run, 15 liters of 1000 mg/l Cr III synthetic solution was prepared according to the method described in section 3.3.1.

#### 3.4.2 Experimental Setup for Phase II

There are four mixing factors affecting the removal of Cr III using CKD or MP. These factors include waste material dose, flash mixing speed ( $G_{fm}$ ), and Camp No. ( $G_{gm}t$ ) which include flocculation (gentle) speed ( $G_{gm}$ ) and flocculation time ( $t$ ) as illustrated in Figure 3.3. However, it is hard to study more than two variables simultaneously. Therefore, to reduce the number of variables studied simultaneously, two pre-tests were conducted to determine the flocculation mixing speed ( $G_{gm}$ ) and the dose of waste materials. Then, the other two variables including flash mixing speed ( $G_{fm}$ ) and flocculation time ( $t$ ), which is reflected on Camp No., were studied at the values of flocculation mixing speed ( $G_{gm}$ ) and initial waste material dose determined by the pre-tests.

##### 3.4.2.1 Pre-test for The Determination of Waste Materials Doses Used in Phase II

The doses of the waste materials that were used in the experiments of phase II were determined based on the ability to clarify the chromium synthetic solution. Jar tests were conducted to determine these doses for both CKD and MP. For CKD, three doses were

tested by the addition of 0.2, 0.5 and 1 g of CKD into 500 ml of Cr III synthetic solution. For MP, five doses were tested by the addition of 1, 3, 5, 8 and 10g into 500 ml of Cr III synthetic solution. The jar tests were conducted using jar tester, manufactured by Phipps & Bird, USA. The following procedure was followed for the jar test for both CKD and MP at different doses:

1. Doses of waste materials were added to the synthetic solutions and flash mixed at speed of 300 RPM for 1 min
2. Gentle mixed at speed of 40 RPM for 10 min
3. The solutions were allowed to settle for 20 min
4. Doses were evaluated visually based on the clarification of the solution

#### *3.4.2.2 Pre-test for Determination of the Flocculation mixing speed ( $G_{gm}$ ) for Phase II experiments*

In this pre-test for phase II experiments, jar test was conducted by adding 1 g of CKD to each of five reactors and 10 g of MP to different five reactors. Each reactor was filled with 500 ml of synthetic Cr III solution at pH of 3.00. After the addition of CKD or MP to Cr III solution, the contents were flash mixed at a speed of 300 RPM for 1 min; then gently mixed at 10, 30, 40, 50 and 60 RPM, respectively, for 10 min. Then, the contents were allowed to settle for 20 min and the solutions were then filtered using cellulose acetate filter paper (0.45  $\mu\text{m}$  pore size). The filtrates were collected for the analysis of trivalent chromium.

#### *3.4.2.3 Effects of Flash Mixing speed and Flocculation Time on the removal of Cr III*

Jar tests were conducted to study the effect of mixing conditions on the removal of Cr III from aqueous solution. For each of the waste materials, CKD and MP, five experimental runs were carried out. Each run was conducted at a specific flash mixing speed ( $G_{fm}$ ) for 1 min. Five  $G_{fm}$  values were studied for both waste materials. These values included 100, 150, 200, 250, 300 RPM, respectively. During each of the experimental runs, five different values of flocculation times were studied at each specific value of  $G_{fm}$ . The tested flocculation times included 10, 20, 30, 40 and 60 min applied at flocculation mixing speed of 40 RPM for CKD and 30 RPM for MP. In all experimental runs, the doses of the

waste materials were 1 g and 10 g for CKD and MP, respectively, and each dose was added to 500 ml of Cr III solution. After flash and flocculation mixing, the contents were allowed to settle for 20 min and the solutions were then filtered using cellulose acetate filter paper (0.45 µm pore size). The filtrates were collected for the analysis of trivalent chromium.

### 3.4.3 Energy Consumption Calculations

Energy consumption in treatment process using chemical coagulation/ precipitation is mainly due to mixing. Therefore, to evaluate the treatment performance of both CKD and MP, the energy consumed in the mixing process for each material was determined. During the experiments, the energy consumed during flash and flocculation mixing, was calculated using equations 3.1 and 3.2.

$$\bullet \quad E = P * t \quad (\text{Eq 3.1})$$

Where:

$E$  = Energy Consumed due to mixing, J

$P$  = Power Consumed due to mixing, N-m/s

$t$  = Time of mixing, s

Power ( $P$ ) is the power transmitted to water. It depends on the flow regime and the impeller type. In this experiment, the impellers used in the jar test were flat paddles with 2 blades for the single paddle and the diameter to width ratio of the impeller  $D_i/W_i$  is equal to 4.0 as shown in Figure 3.4. In addition, from the results obtained from eq 3.3, the flow is turbulent for all the rotational speeds used in this experiment. So, according to Reynolds & Richard, (1996), the impeller constant for turbulent flow ( $K_T$ ) in eq 3.2 is equal to 2.25. Equation 3.2 was used to calculate the power ( $P$ ):

$$P = K_T * n^3 * D_i^5 * \rho \quad (\text{Eq. 3.2})$$

Where:

$P$  = Power due to mixing, N-m/s

$K_T$  = impeller constant = 2.25 for turbulent flow

$n$  = rotational speed, rps

$D_i$  = impeller diameter, m

$\rho$  = density of water at 25 °C, 1000 kg/m<sup>3</sup>

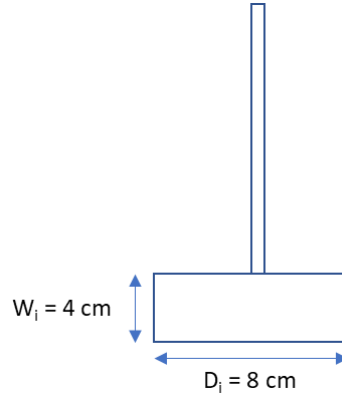


Figure 3.4: Schematic Diagram for the Impeller Used in the phases II, III and IV

The regime of flow can be determined using Reynolds number ( $N_{Re}$ ). Equation 3.3 is used to determine Reynolds number in order to identify if the flow regi

me is laminar, for  $N_{Re} < 10$  to 20, or turbulent, for  $N_{Re} > 10,000$ .

$$N_{Re} = (D_i^2 * n * \rho) / \mu \quad (\text{Eq. 3.3})$$

Where:

$N_{Re}$  = Reynolds Number

$D_i$  = impeller diameter, (m)

$n$  = rotational speed, (rps)

$\rho$  = density of water at 25 °C, 1000 kg/m<sup>3</sup>

$\mu$  = absolute viscosity of water at 25 °C,  $8.90 \times 10^{-4}$  Pa.s

#### 3.4.4 Velocity Gradient Calculations

As Reynolds number and the power consumed during flash and flocculation mixing were calculated using Eq. 3.1 and Eq. 3.2. The velocity gradient for each rotational speed used in flash and flocculation mixing was calculated using the following equation:

$$G = \sqrt{\frac{P}{\mu * V}} \quad (\text{Eq. 3.4})$$

G = Velocity gradient, s<sup>-1</sup>

P = Power, N-m/s

μ = Absolute viscosity of water at 25 °C, 8.90 × 10<sup>-4</sup> Pa.s

V = Volume, m<sup>3</sup>

### 3.5 Phase III: Identifying Optimum Operating Conditions

The experiments in phase III was divided into two main parts. In the first part, the optimum operating conditions were studied for the removal of Cr III using CKD. In the second part, a comparison between the performance of CKD and reference common precipitants were investigated. The mixing conditions obtained from phase II were used in the experiments of phases III and IV.

#### 3.5.1 Phase III - Part I: Effect of CKD dose and Cr III initial concentration

This part of phase III was conducted using jar test over five experimental runs with synthetic trivalent chromium solutions with five different initial Cr III concentrations. Guo et al., 2006 indicated that Cr III concentration in tanneries wastewater in China ranges from 3000 to 6000 mg/l. Another work, Esmaeili et al. 2005 indicated that Cr III concentration in tanneries wastewater ranges from 3250 to 5300 mg/l. In Egypt, Abdulla & Ahmed, 2010 collected samples from tanneries in Old Cairo and the Cr III concentration in the collected samples ranged from 1625 to 2410 mg/l. Therefore, in the current part of phase III, the effect of initial Cr III concentration on the removal of Cr III removal was studied. Five values of initial Cr III concentration, that covered the ranges reported in the literature, were tested in this part of phase III. These values include initial Cr III concentrations of 500, 1000, 3000, 5000 and 6000 mg/l. For each value of initial Cr III concentrations, six different CKD doses were tested. These doses include 0.5, 1, 3, 5, 10 and 20 g CKD per 500 ml.



#### *3.5.1.1 Synthetic solution preparation*

In this part of phase III, synthetic solutions, with Cr III initial concentrations of 500, 1000, 3000, 5000 and 6000 mg/l, were used to study the effects of initial Cr III concentration and CKD dose on the removal of Cr III. These solutions were prepared by weighing 20.838, 17.365, 10.419, 3.473 and 1.736 mg of hydrate chromium (III) sulfate ( $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ ) and each of these amounts was dissolved in 500 ml of distilled water and completed to 1000 ml using distilled water in order to prepare synthetic solutions with concentrations of 6000, 5000, 3000, 1000 and 500 mg/l, respectively. The pH value for all concentrations was adjusted to 3.00 using 4 M NaOH solution and/or 4 M  $\text{HNO}_3$ .

#### *3.5.1.2 Experimental Setup*

Jar tests were conducted over five experimental runs to study the effect of initial Cr III concentration and CKD dose on the removal of Cr III. Each run was conducted at a specific initial Cr III concentration.

During each of the experimental runs, six different CKD doses were added to 500 ml of synthetic solution with the specific initial Cr III concentration. They were flash mixed on the jar tester at speed of 150 RPM for 1 min followed by slow mixing at speed 40 RPM for 20 min. Then the solutions were kept for settling for 20 min. After that, the contents were filtered using cellulose acetate filter paper (0.45  $\mu\text{m}$  pore size) and the filtrates were collected for Cr III concentration analysis.

### **3.5.2 Phase III - Part II: CKD Versus Reference Precipitants for the Removal of Cr III**

In part II of phase III, two types of common precipitants, magnesium oxide ( $\text{MgO}$ ) and sodium hydroxide ( $\text{NaOH}$ ) were used to precipitate Cr III from synthetic solution and the results were compared with CKD.

For the experiments in part II in phase III, eleven reactors were filled with 500 ml of synthetic Cr III solution with initial concentration of 1000 mg/l and pH value of 3.0. Magnesium oxide ( $\text{MgO}$ ) was added at different doses to six of these reactors, while sodium hydroxide ( $\text{NaOH}$ ) was added to the remaining five reactors. Jar test was performed

on these reactors as explained in part I of phase III. Magnesium oxide was added at similar doses to these of CKD namely 0.5, 1, 3, 5, 10 and 20 g per 500 ml of Cr III solution. On the other hand, five different doses of 1M NaOH solution were added to the remaining five reactors. These doses include 2.1, 9.4, 12.5, 15.5 and 19.6 ml per 500 ml of Cr III solution.

### **3.6 Phase IV: Testing of Real Tannery wastewater**

In this phase, the optimum mixing and operating conditions obtained from phases II and III were applied on real tannery wastewater samples. The samples were collected from a tannery located in Quesna, Monofia Governorate, Egypt.

#### **3.6.1 Properties of Tannery Wastewater**

Before starting the experiment, it was important to identify the wastewater properties, which include Cr III concentration, biological oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD) and total suspended solids TSS, by conducting the following tests:

- Chemical oxygen demand (COD) was analyzed using HACH method number 8000 for HACH DR/2000 spectrophotometer
- Biological oxygen demand (BOD<sub>5</sub>) was analyzed using method number 5210B in the Standard Methods for the examination of water and wastewater (APHA, AWWA and WEF 1992)
- Total suspended solids (TSS) was analyzed using method number 2540D in the Standard Methods for the examination of water and wastewater (APHA, AWWA and WEF 1992)
- Turbidity was analyzed using HACH method number 8237 for HACH DR/2000 spectrophotometer

#### **3.6.2 Experimental procedure**

As will be discussed later, Cr III concentration of the real samples of tannery wastewater was much higher than the range that had been tested in phase III. As a result, experiments were conducted in order to determine the optimum dose of CKD that can remove Cr III and the effect of this dose on the other properties.

So, five reactors were filled with 500 ml of tannery wastewater, then five different doses of CKD include 10, 15, 20, 25 and 30 g of CKD were added. Then, the contents were flash mixed for 1 min at speed of 150 RPM followed by flocculation mixing at 40 RPM for 20 min, then the solutions were kept for settling 20 min. After that, the solutions were filtered using cellulose acetate filter paper (0.45  $\mu\text{m}$  pore size) and the filtrates were collected for Cr III concentration analysis.

### 3.6.3 Characterization of the Precipitated Sludge

In order to prepare the precipitated sludge, a reactor was filled of 500ml wastewater and 25g CKD were added. The reactor was placed on the jar tester and flash mixed for a minute at speed of 150 RPM followed by slow mixing at 40 RPM for 20 min. Then, the mixture was filtered and kept for thickening for 24 hours on a 0.7  $\mu\text{m}$  glass fiber filter paper; then dried in the oven at 80°C till complete dryness. The resulted complete dry precipitated sludge was weighed and the amount of chromium III in the sludge was calculated.

## 3.7 Phase V: Chromium Recovery from Precipitates due to Treatment

During this phase, sulfuric acid solution was used in order to recover trivalent chromium as chromium sulfate from the precipitated sludge resulted from the tannery wastewater treatment. In order to have better understanding of the recovery process and the conditions that affect its efficiency, this phase was divided into three parts. In the first part, the reaction time for the best recovery was determined and, in the second part, the effect of the concentration of the extraction solution was investigated, finally, the third part included investigating the effect of the  $\text{H}_2\text{SO}_4$  volume/weight of sludge percentage (v/w) on the efficiency of recovery.

### 3.7.1 Phase V - Part I: Effect of Reaction Time

To evaluate the effect of reaction time on the efficiency of recovery, these experiments were conducted over five runs with five different reaction times using extraction solution with  $\text{H}_2\text{SO}_4$  concentration of 2.72%.

#### *3.7.1.1 Extraction Solution Preparation*

To prepare the extraction solution used in this part, 14 ml of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was dissolved in 500 ml of distilled water. As sulfuric acid is a very strong diprotic acid, it was dissolved carefully in 25 ml of distilled water then the remaining amount of water was added gradually.

#### *3.7.1.2 Experimental setup*

To evaluate the effect of the reaction time and determine the optimum reaction time for chromium recovery, these experiments were conducted over five different reaction times, included 10, 20, 40, 60 and 120 min.

Five glass beakers were filled with 514 ml of the extraction solution with 2.72%  $\text{H}_2\text{SO}_4$  and 5g of complete dry precipitated sludge, prepared according to the method described in section 3.6.3, and placed on magnetic stirrer. The solutions were mixed at medium speed for 10, 20, 40, 60 and 120 min. Then, the solutions were filtered using cellulose acetate filter paper (0.45  $\mu\text{m}$  pore size) and the filtrates were collected for Cr III concentration analysis.

### *3.7.2 Phase V - Part II: Effect of $\text{H}_2\text{SO}_4$ Concentration on Recovery*

In this part, extraction solutions with five different  $\text{H}_2\text{SO}_4$  concentrations were used to extract chromium III from five different loads of sludge in order to evaluate the effect of the concentration of the extraction solution and the load of the sludge on the efficiency of chromium recovery. As will be discussed later, the reaction time used in these experiments was the optimum reaction time obtained from the previous part which was 120 min.

#### *3.7.2.1 Extraction Solutions Preparation*

Five extraction solutions with concentrations 1.19, 2.72, 5.3, 7.75 and 10.07% of  $\text{H}_2\text{SO}_4$  were prepared by dissolving 6, 14, 28, 42 and 56 ml of concentrated  $\text{H}_2\text{SO}_4$  in 500 ml of water. The precautions mentioned in section 3.7.1.1 should be taken in consideration.

### 3.7.2.2 *Experimental Setup*

These experiments were divided into five experimental runs with five different sludge loads. The sludge weighs used in these experiments included 2.5, 5, 10, 20 and 30g of the sludge. In each experimental run, five beakers were filled with the extraction solutions with volumes of 506, 514, 528, 542, and 556 ml. One of the five sludge loads mentioned before was added to the five beakers and mixed at medium speed using magnetic stirrer for 120 min. Then, the solutions were filtered using cellulose acetate filter paper (0.45  $\mu\text{m}$  pore size) and the filtrates were collected for Cr III concentration analysis.

### 3.7.3 Phase V - Part III: Effect of the percentage of Sulfuric Acid Volume to the Weight of the Sludge

In this part, in order to evaluate the effect of the percentage sulfuric acid ( $\text{H}_2\text{SO}_4$ ) volume to the weight of the sludge (v/w) on the recovery efficiency, different amounts of the complete dry sludge were dissolved in extraction solutions with different concentrated ( $\text{H}_2\text{SO}_4$ ) volumes.

#### 3.7.3.1 *Experimental Set up*

These experiments were conducted over three experimental runs with three different sludge loads. In each experimental run five different percentages of  $\text{H}_2\text{SO}_4$  volume and sludge weight (v/w) were used included 0.2, 0.6, 1.4, 5.6 and 11.2 ml/g. In the first trial, 0.5, 1.5, 3.5, 14 and 28 ml of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were completed to 500 ml using distilled water in 500 ml beakers. Then, 2.5g of dry sludge were weighed and added to each beaker; then the mixture in each beaker was stirred at medium speed for 120 min. In the second trial, 0.2, 0.6, 1.4, 5.6 and 11.2 ml of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were completed to 50 ml using distilled water in 200 ml beakers. Then, 1g of dry sludge were weighed and added to each beaker; then the mixture in each beaker was stirred at medium speed for 120 min. In the third trial, 0.6, 1.8, 4.2, 16.8 and 33.6 ml of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were completed to 50 ml using distilled water in 200 ml beakers. Then, 3 g of dry sludge were weighed and added to each beaker; then the mixture in each beaker was stirred at medium speed for 120 min. In all runs, after stirring,

the recovered chromium sulfate ( $\text{Cr}_2(\text{SO}_4)_3$ ) solution was filtered on cellulose acetate filter paper (0.45  $\mu\text{m}$  pore size) and collected for Cr III concentration analysis.

### **3.8 Trivalent Chromium Analysis Method Using Flame Atomic Absorption Spectrometry**

The analysis method during all experiments depended on using flame atomic absorption spectrometry instrument to directly analyze the trivalent chromium concentration. In order to apply this method, a stock of trivalent chromium solution was prepared by dissolving 3.473 of chromium trivalent sulfate ( $\text{Cr}_2(\text{H}_2\text{SO}_4)_3$ ) in 1000 ml of distilled water; then five standard chromium solutions with concentrations of 5, 10, 15, 20, and 30 mg/l were prepared by diluting 0.5, 1, 1.5, 2 and 3 ml of a stock to 100 ml using distilled water. These standard solutions were placed and run in the flame atomic absorption in order to determine their absorbance, then a five-points liner calibration curve was established. After placing and running zero concentration and blank samples, the atomic spectrometer was ready to directly analysis trivalent chromium samples with concentrations less than 30mg/l.

## Chapter 4: Results and Discussion

### 4.1 Performance of Different Waste Materials

A comparative experiment was conducted for two groups of solid wastes. The first group was organic solid wastes group which included rice straw (RS), rice husk (RS), sugarcane bagasse (SB) and sawdust (SD), on the other hand, the second group was inorganic solid wastes group which included cement bypass kiln dust (CKD) and marble powder (MP). The experiment was conducted under the following conditions:

- $\text{Cr}^{+3}$  Concentration = 1000 mg/l
- pH of the Solution = 3.00
- Solution Volume = 50 ml
- Shaking Time = 60 min
- Speed of Shaking = 200 RPM
- Temperature = room temperature (23°C)

According to the results of this phase shown in Table 4–1 and illustrated in Figure 4.1, there is a great gap between the removal efficiencies of organic solid wastes and inorganic solid wastes. For the organic solid wastes, the removal efficiency ranges from 0.4 to 13.3 % and the highest percentage was recorded for the rice straw which was 13.3%. On the other side, the inorganic solid wastes recorded removal efficiencies of 99.9% for CKD and 98.8% for MP. This gap can be related to the observed differences in the pH values of the solution, which illustrated in Figure 4.2, that occurred after the treatment process. It can be noticed that both CKD and MP raised the alkalinity of the solution after the treatment to 7.78 and 7.13, respectively.

Table 4-1: Phase I experimental results

Waste Material	Trials No.	Initial conc. (mg/l)	Final Conc. (mg/l)	Initial pH	Final pH	Removal Efficiency (%)
Rice Husk (RH)	3	1000	878.5	3.00	3.77	12.2
Rice Straw (RS)	3	1000	867.4	3.00	3.87	13.3
Sugarcane Bagasse (SB)	3	1000	968.2	3.00	2.96	3.2
Sawdust (SD)	3	1000	995.7	3.00	2.89	0.4
Cement bypass kiln dust (CKD)	3	1000	1.4	3.00	7.78	99.9
Marble Powder (MP)	3	1000	12.4	3.00	7.13	98.8
Control	3	1000	995.65	3.00	2.52	0.4

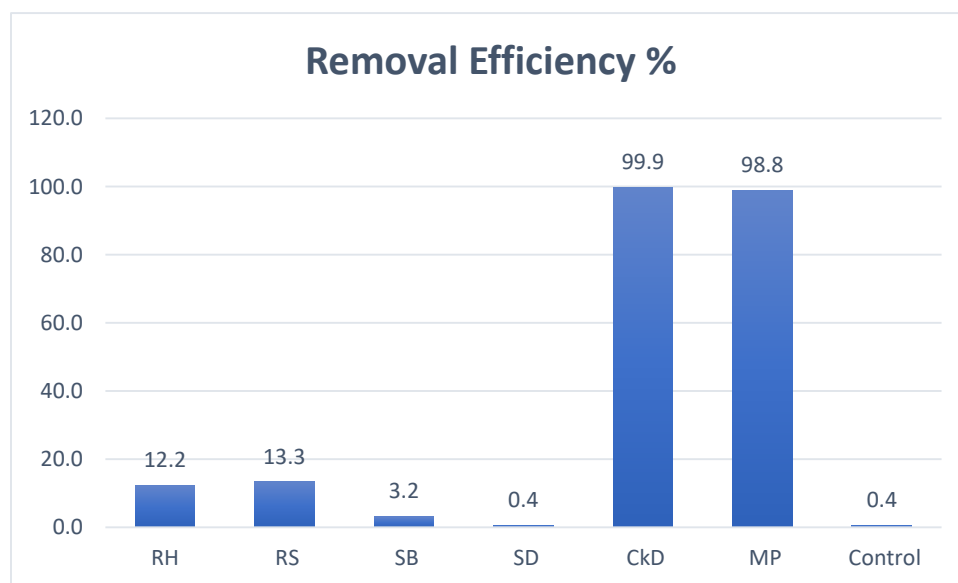


Figure 4.1: Solid Wastes Removal Efficiencies



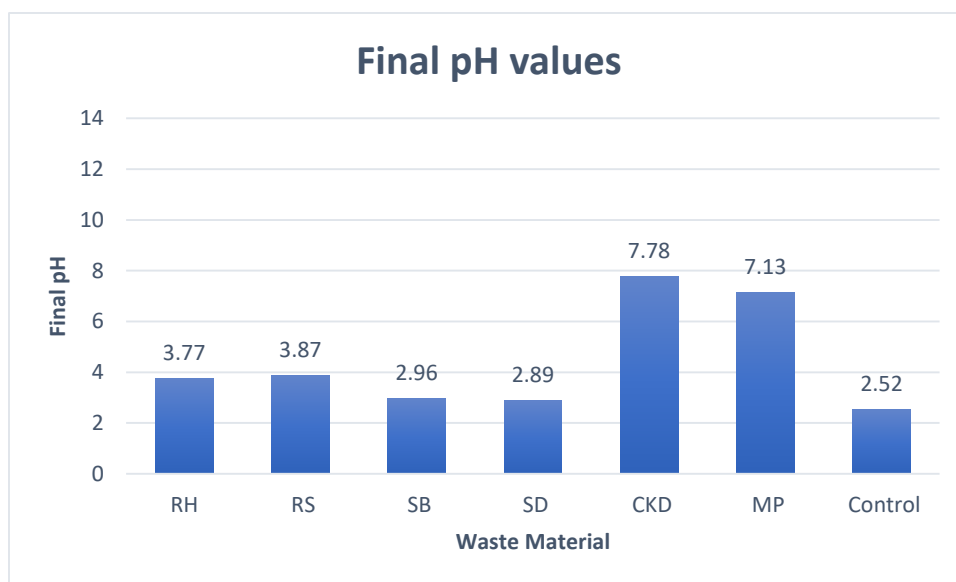


Figure 4.2: Final pH values for treated solutions

According to Unceta et al, 2010, Cr III precipitates as chromium hydroxide ( $\text{Cr}(\text{OH})_3$ ) after pH 6.00, so, studying the removal efficiency results in parallel with the pH value results, it can be concluded that the removal mechanism of MP and CKD is closer to be precipitation. This mechanism is different than the treatment mechanism of the organic solid wastes which is based on adsorption mechanism (Amer, 2015; Ding et al, 2012; and Rocha et al, 2009). This assumption could be enhanced by the observation in the lab when the solutions treated by cement bypass kiln dust and rice straw were kept settling for 20 min. As shown in Figure 4.3, unlike the solution treated by rice straw, the solution treated by cement bypass kiln dust created a grayish green precipitated which is different than the cement bypass kiln dust residues at the bottom of the volumetric cylinder as shown in Figure 4.4. Also, the same results were obtained in case of using MP.



Figure 4.3: Rice Straw and Cement bypass kiln dust Treatment

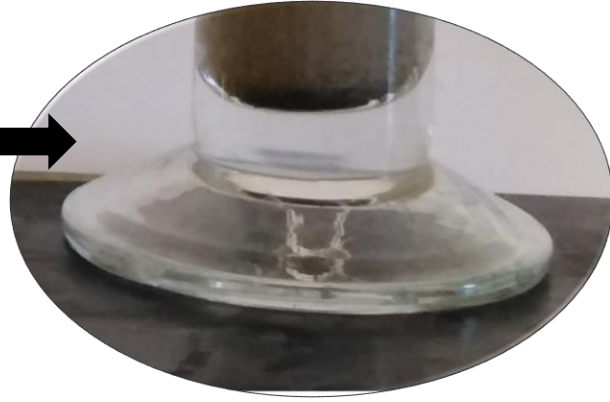


Figure 4.4: Cement bypass kiln dust Residue

#### 4.1.1 Material Selection According to Wastes Performance

According to the previous discussion, the inorganic solid wastes showed better removal efficiency and performance. The removal efficiency for CKD reached 99.9% and for MP reached 98.8%. These results are very promising taking in consideration the increase in these two waste materials in the recent years due to the increasing in the construction development that Egypt witnesses lately. Consequently, cement bypass kiln dust and marble powder were chosen to be studied in the next phase.

### 4.2 Identifying Flocculation mixing speed ( $G_{sm}$ ) and Material Dose

As explained in section 3.4.2, two pretests were conducted to identify the dose that can be used in evaluating the mixing conditions for both cement bypass kiln dust and marble powder. So, in the following lines, the results of these pretests will be discussed.

#### 4.2.1 Visual Effect of the CKD and MP Doses

In order to determine the suitable dose that can be used to evaluate the mixing conditions, pretest was conducted to identify the dose of cement bypass kiln dust and marble powder at which the solution starts to clarify. According to visual observations, cement bypass kiln dust started to clarify the solution at dose of 1g/ 500 ml as shown in Figure 4.5; however, as shown in Figure 4.6, marble powder couldn't clarify the solution till the dose reached 10g/ 500 ml.

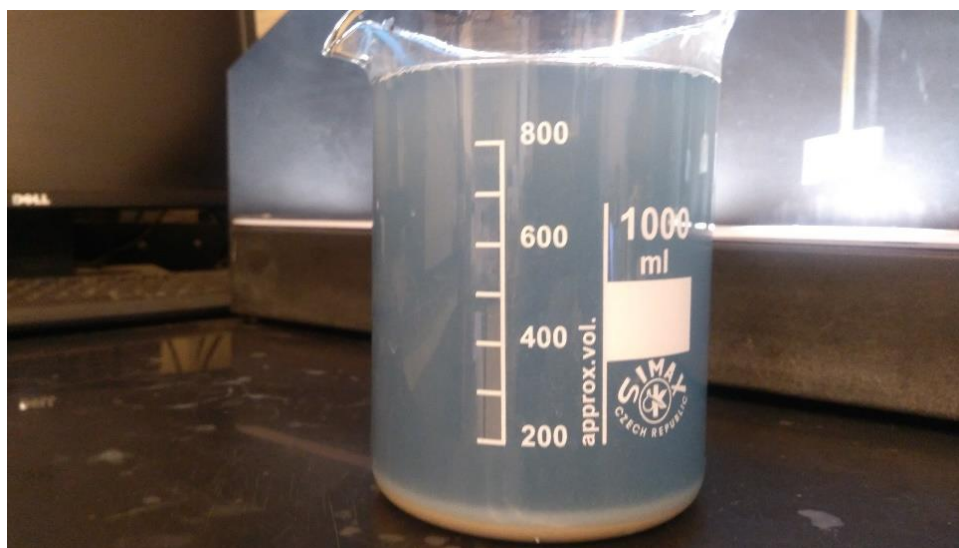


Figure 4.5: Effect of 1g CKD on the Color of the Solution



Figure 4.6: Effect of MP dosages on the Color of the Solution

#### 4.2.2 Effect of Flocculation mixing speed

In order to identify the optimum flocculation mixing speed that can be used in the rest of the study, a pretest was conducted under the following conditions:

- $\text{Cr}^{+3}$  concentration = 1000 mg/l
- pH of the solution = 3.00
- Solution volume = 500 ml
- Weight of CKD = 1g
- Weight of MP= 10g
- Temperature= room temperature (23 °C)

According to the results shown in Table 4–2 and Figure 4.7, removal efficiency of Cr III for both cement bypass kiln dust and marble powder increased by increasing the flocculation mixing speed ( $G_{gm}$ ) till it reached the maximum value at certain speed then it remained constant in case of CKD, and started to decrease in case of MP. The decrease in the removal efficiency of Cr III, in case of MP, can be explained as the flocs formed is fragile so it breaks down due to the increase in the flocculation mixing speed (Reynolds & Richard, 1996; Sánchez-Martín et al., 2012). The maximum removal efficiency of Cr III was 99.96% for CKD recorded at flocculation mixing speed of 40 RPM; while the maximum removal efficiency of Cr III for marble powder was 98.07% recorder at flocculation mixing speed of 30 RPM. Based on these results the flocculation mixing speed used in evaluating the mixing conditions was 40 RPM for cement bypass kiln dust and 30 RPM for marble powder.

Table 4-2:  $G_{gm}$  Pretest Results for CKD and MP

Material	Flocc. Speed (RPM)	Initial pH	Final pH	Initial Conc. (mg/l)	Final Conc. (mg/l)	Removal Efficiency %
CKD	10	3	7.48	1000	15.15	97.84
	30	3	7.62	1000	1.368	99.90
	40	3	7.78	1000	0.279	99.96
	50	3	8.03	1000	0.458	99.95
	70	3	8.18	1000	0.563	99.95
MP	10	3	5.57	1000	159.70	84.03
	30	3	6.11	1000	19.32	98.07
	40	3	6.24	1000	26.30	97.37
	50	3	6.14	1000	115.81	88.42
	70	3	6.24	1000	127.70	87.23

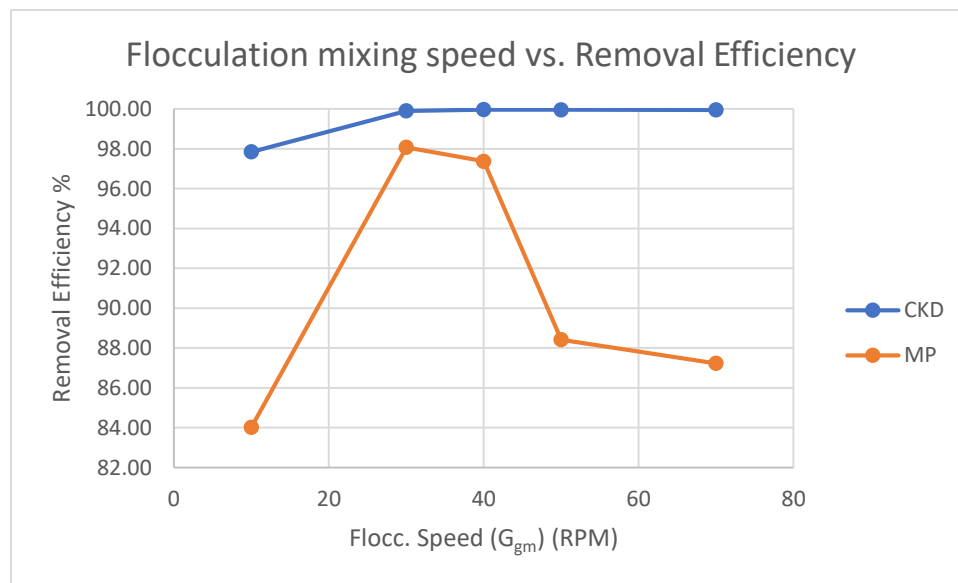


Figure 4.7: Flocculation mixing speed ( $G_{fm}$ ) vs. Removal Efficiency for CKD and MP (initial pH = 3.00)

### 4.3 Effect of Mixing on the Performance of Cement bypass kiln dust (CKD) and Marple Powder (MP) in Chromium Removal

Based on the results of phase I, the inorganic solid wastes showed excellent performance in Cr III removal. As a result, jar-test experiments were conducted in phase II to study the relationship between removal efficiencies, flash mixing speeds ( $G_{fm}$ ), and both flocculation mixing speed and time ( $G_{gmt}$ ) or what is called by Camp No. According to the

results of the pretests, the suitable dose that could be used for CKD was 1g/500ml and 10g/500ml for MP; on the other hand, the optimum flocculation mixing speed to be used was 40 RPM, for CKD, and 30 RPM for MP. Based on these results, jar-test experiments were conducted under the following conditions:

- $\text{Cr}^{+3}$  concentration = 1000 mg/l
- pH of the solution = 3.00
- Solution volume = 500 ml
- Weight of CKD = 1g
- Weight of MP= 10g
- Temperature = room temperature (23°C)
- Slow mixing speed for MP = 30 RPM
- Slow mixing speed for CKD = 40 RPM

According to the calculations based on equations 3.1, 3.2 and 3.3, the parameters and results, shown in Table 4–3, were obtained which were used to help in comparing the efficiencies of the treatment using marble powder (MP) and cement bypass kiln dust (CKD).

*Table 4–3: Important Parameters*

<b>n (RPM)</b>	<b>n (rps)</b>	<b><math>N_{re}</math></b>	<b>P (N-m/s)</b>	<b>G (<math>s^{-1}</math>)</b>
<b>300</b>	5.00	2157303	0.9216	1439.10
<b>250</b>	4.17	1797753	0.5333	1094.76
<b>200</b>	3.33	1438202	0.2731	783.35
<b>150</b>	2.50	1078652	0.1152	508.80
<b>100</b>	1.67	719101.1	0.0341	276.96
<b>40</b>	0.67	287640.4	0.0022	70.06
<b>30</b>	0.50	215730.3	0.0009	45.51

Through the experiments conducted during this phase, it can be observed that there are some differences between the treatment process for cement bypass kiln dust (CKD) and marble powder (MP). The treatment performance of both materials is almost similar; however, the treatment conditions are different as illustrated in the following lines.

#### 4.3.1 Cement bypass kiln dust

As illustrated in the previous lines, chromium solution with initial concentration 1000 mg/l and pH value 3.00 was treated using 1g of cement bypass kiln dust (CKD) over several flash-mixing speeds, several flocculation time-periods and with 40 RPM ( $70.06\text{s}^{-1}$ ) flocculation mixing speed. According to the results presented in Table 4–4, the final concentrations for all experiments ranged from 0.1 to 5.4 mg/l which means that the treatment efficiency for all speeds and flocculation times exceed the 99%.

Table 4-4:  $G_{fm}$  and  $G_{gmt}$  values results for CKD:

$G_{fm} (s^{-1})$	Flocc. Time (t)	$G_{gmt}$	Final pH	final Conc. (mg/l)	Removal Efficiency %
<b>1439.1</b>	10	42036	9.11	2.864	99.71
	20	84072	9.82	1.756	99.82
	30	126108	9.59	1.245	99.88
	40	168144	10.02	1.393	99.86
	60	252216	10.14	2.315	99.77
<b>1094.76</b>	10	42036	9.09	2.607	99.74
	20	84072	9.73	1.601	99.84
	30	126108	10.02	1.057	99.89
	40	168144	9.95	1.136	99.89
	60	252216	10.44	1.762	99.82
<b>783.35</b>	10	42036	10.36	2.357	99.76
	20	84072	9.91	1.490	99.85
	30	126108	10.51	1.085	99.89
	40	168144	10.51	1.375	99.86
	60	252216	9.84	3.373	99.66
<b>508.8</b>	10	42036	9.45	1.520	99.85
	20	84072	10.23	0.102	99.99
	30	126108	10.13	0.122	99.99
	40	168144	10.30	2.015	99.80
	60	252216	10.12	3.294	99.67
<b>276.96</b>	10	42036	7.23	5.405	99.46
	20	84072	9.20	3.711	99.63
	30	126108	7.91	3.292	99.67
	40	168144	9.24	2.203	99.78
	60	252216	9.20	2.181	99.78

However, the removal efficiency slightly differentiated with the change of flash mixing speed ( $G_{fm}$ ). It can be observed from Figure 4.8 that, generally, the average removal efficiency of CKD increased by decreasing the flash mixing speed till it reaches 100% at 150 RPM ( $508.8 s^{-1}$ ) then the efficiency slightly decreased to be 99.4% at 100 RPM ( $276.96 s^{-1}$ ).



From the other side, by having closer look at the behavior of the removal efficiencies for each flash mixing speed with the change of Camp No. by changing the flocculation time, it can be observed that the removal efficiency increased by increasing the flocculation time, then this behavior changed after certain value for Camp No.; however, this value changes from flash mixing speed to another. For more illustration, having an example of flash mixing speed 150 RPM ( $508.8 \text{ s}^{-1}$ ), the removal efficiency increased by increasing the flocculation time to 20 min to reach 99.99% then started to decrease after that to reach 99.67% at 60 min of flocculation.

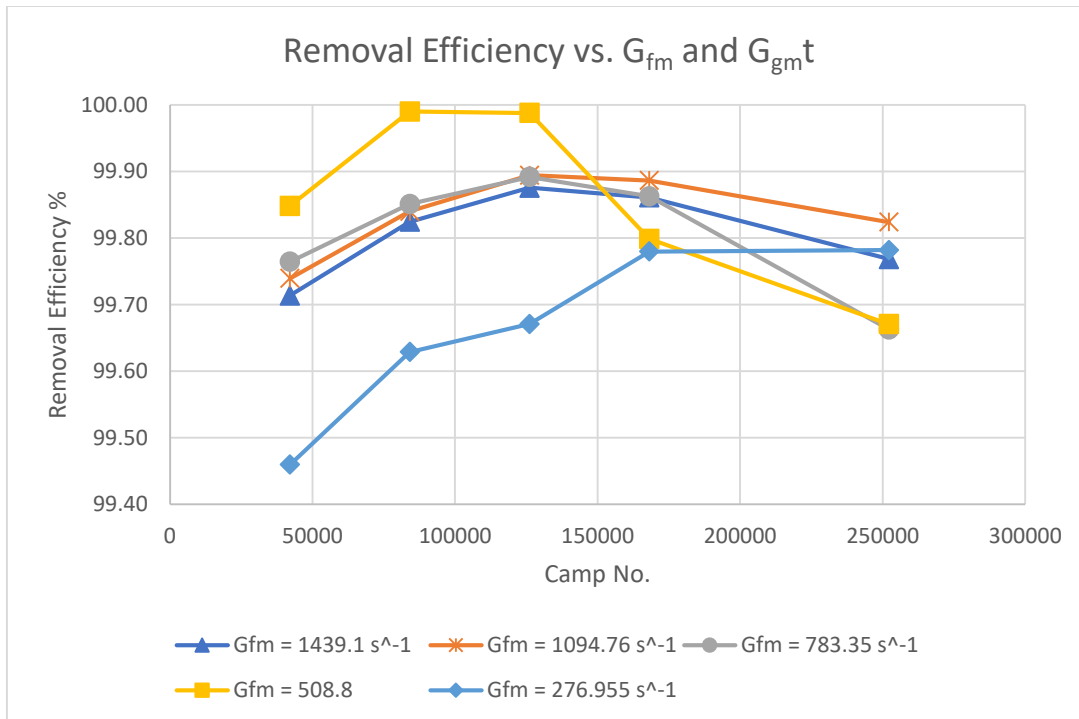


Figure 4.8: Removal Efficiencies for  $G_{fm}$  and  $G_{gm} t$  Values (initial pH= 3.00)

According to the results in Table 4–4, it can be observed that there is a relationship between the pH value of the solution,  $G_{fm}$  and  $G_{gmt}$  values, and the removal efficiency of Cr III using CKD. As illustrated in Figure 4.9, the pH value of the solution increased by increasing the flash mixing speed and Camp No.; that is because the increase in the speed and flocculation time gives the cement bypass kiln dust bigger chance to react with the solution. Also, it can be observed that the increase in the removal efficiency of Cr III was parallel to the increase in the alkalinity of the solution. This observation gives a strong hint

that the treatment mechanism is close to chemical precipitation which is depending on increasing the alkalinity of the solution.

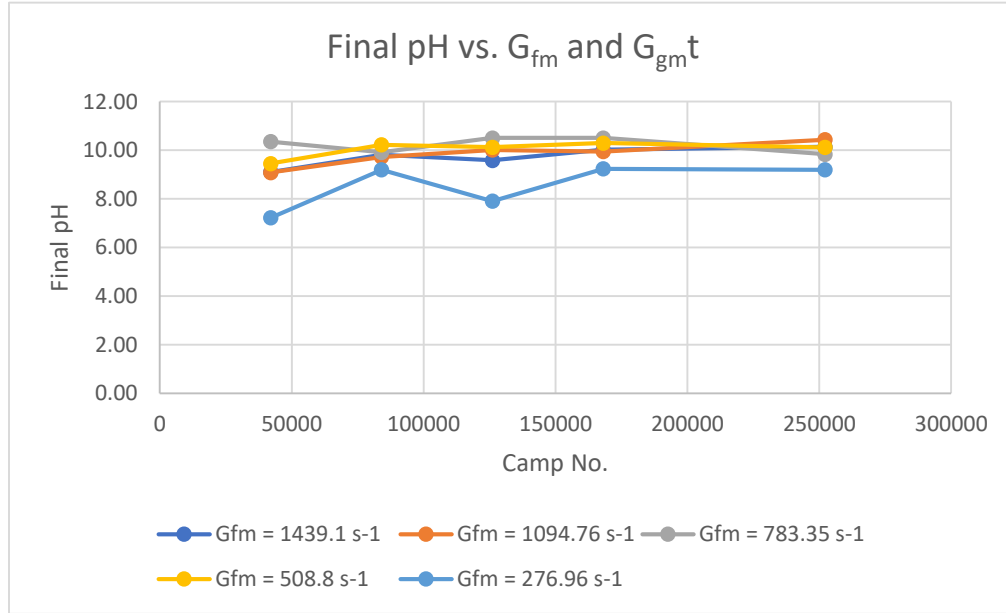


Figure 4.9: pH values vs.  $G_{fm}$  and  $G_{gm} t$  (CKD) (initial pH= 3.00)

#### 4.3.2 Marble Powder (MP)

Unlike the case of cement bypass kiln dust (CKD), chromium solution with initial concentration 1000 mg/l with pH value 3.00 was treated using 10g of marble powder using the same flash mixing speeds and flocculation times used for CKD but with 30 RPM ( $45.51 \text{ s}^{-1}$ ) flocculation mixing speed. According to the results presented in Table 4–5, the final concentrations for all experiments ranged from 11.76 to 341.75 mg/l which means that the treatment efficiency for all speeds and flocculation time periods ranged from 65.83 to 98.82%.

Table 4-5:  $G_{fm}$  and  $G_{gm} t$  values results for MP

$G_{fm} (s^{-1})$	Flocc. Time (min)	$G_{gm} t$	Final pH	final Conc. (mg/l)	Removal Efficiency %
<b>1439.1</b>	10	27306	6.15	49.683	95.03
	20	54612	6.40	35.450	96.46
	30	81918	6.37	42.258	95.77
	40	109224	6.49	35.167	96.48
	60	163836	6.76	33.283	96.67
<b>1094.76</b>	10	27306	5.95	51.365	94.86
	20	54612	6.26	22.420	97.76
	30	81918	6.43	20.207	97.98
	40	109224	6.58	15.183	98.48
	60	163836	6.77	11.762	98.82
<b>783.35</b>	10	27306	6.03	70.375	92.96
	20	54612	6.34	40.292	95.97
	30	81918	6.49	32.475	96.75
	40	109224	6.61	28.292	97.17
	60	163836	6.76	26.225	97.38
<b>508.8</b>	10	27306	5.43	256.463	74.35
	20	54612	5.80	148.992	85.10
	30	81918	5.95	72.450	92.76
	40	109224	6.20	59.200	94.08
	60	163836	6.53	36.325	96.37
<b>276.96</b>	10	27306	5.35	341.7467	65.83
	20	54612	5.46	272.63	72.74
	30	81918	5.72	136.7267	86.33
	40	109224	5.73	131.75	86.83
	60	163836	5.76	129.6083	87.04

By studying the treatment performance according to the change in the flash mixing speed and the Camp No. ( $G_{gm} t$ ) as shown in Figure 4.10, it can be observed that the removal efficiency of Cr III using marble powder (MP) was directly proportional to the Camp No., that is explaining the increase in the removal efficiency by increasing the flocculation time. On the other hand, MP removal efficiency was directly proportional to the flash mixing speed ( $G_{fm}$ ) till it reached its maximum value of 98.82% at gradient velocity value of 1049.76  $s^{-1}$  then it started to decrease by increasing the speed to 1439.1  $s^{-1}$ .

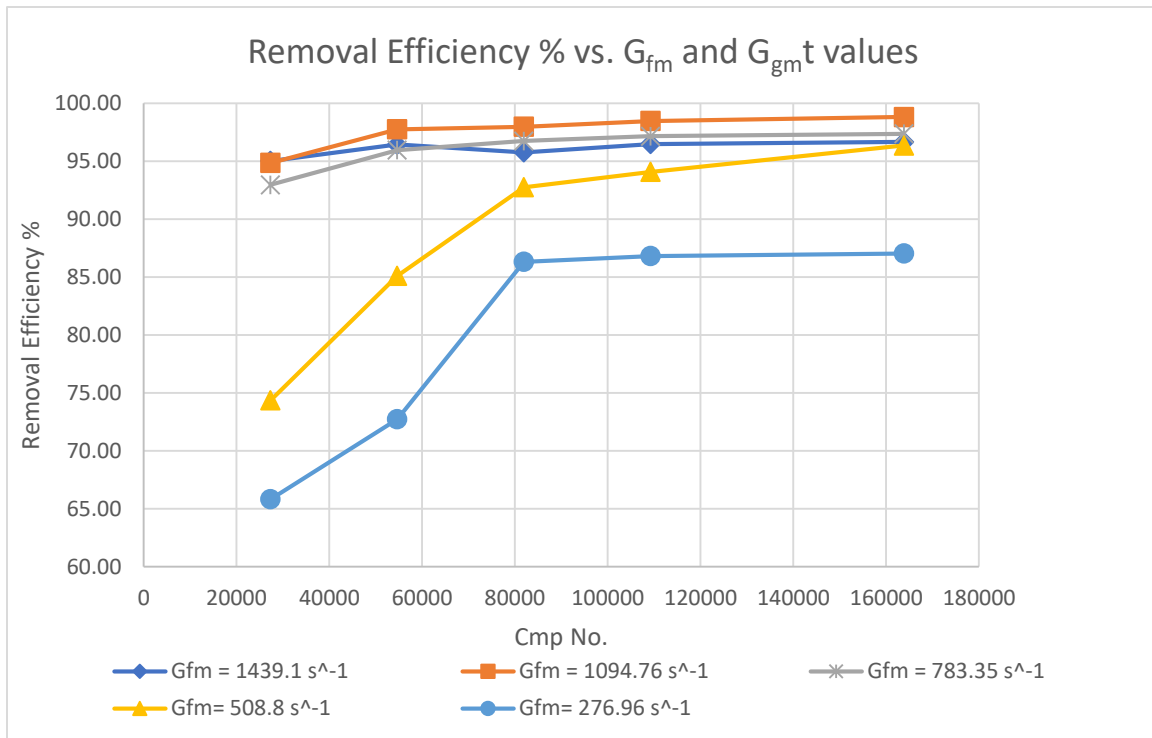


Figure 4.10: Removal efficiency vs.  $G_{fm}$  and  $G_{gmt}$  for MP (initial pH= 3.00)

In addition, studying Figure 4.11, it can be observed the direct proportion relationship between the pH value of the solution and the values of  $G_{fm}$  and  $G_{gmt}$ . This relationship can also explain the removal efficiencies obtained; the increase of the pH values is parallel to the increase in the removal efficiencies which is similar to the performance of the results obtained in the case of CKD. According to this observation, it can be concluded that the treatment mechanism of marble powder (MP) is similar to the treatment mechanism of CKD.

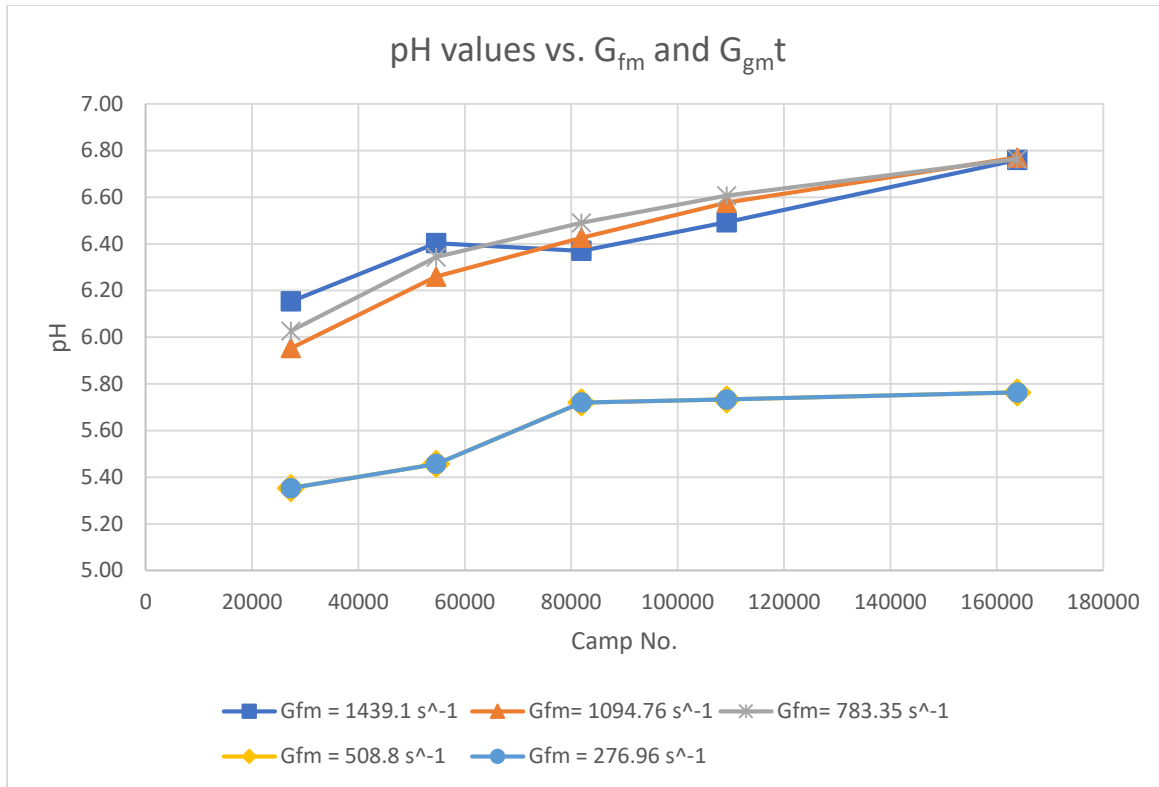


Figure 4.11: pH values vs  $G_{fm}$  and  $G_{gm} t$  for (MP) (initial pH= 3.00)

#### 4.4 Comparison Between Cement bypass kiln dust (CKD) and Marble Powder According to Energy Consumption Due to Mixing

According to Camp, 1955, the mixing degree is depending on the power imparted to the water and he measured this power by the velocity gradient term. And according to the results obtained from this phase, it can be realized that the mixing conditions affected the removal efficiency of both CKD and MP. However, in order to compare the energy consumption due to the power imparted to water in both cases, the energy consumption due to the power imparted to water for the best removal efficiencies for both CKD and MP were calculated as shown in Table 4–6. Studying the results illustrated in Figure 4.12 and Figure 4.13, it can be observed that the energy consumed in the case of using CKD to reach its maximum removal efficiency is smaller than the energy consumed in case of MP to reach its maximum removal efficiency. In case of using CKD, the maximum efficiency was 99.99% obtained by consuming a total energy of 11.25 J; however, in case of using MP, the maximum efficiency was 98.82% obtained by consuming 35.32 J.

Table 4–6: Removal efficiency and Total energy for CKD and MP

Removal material	G (s <sup>-1</sup> )	Energy for G (J)	Final Conc. (mg/l)	Flocc. time (s)	Gt	Energy for Gt (J)	Total Energy (J)	Removal Efficiency %
CKD	1439.10	55.30	1.245	1800	126108	1.083	56.38	99.88
	1094.76	32.00	1.056	1800	126108	2.167	34.17	99.89
	783.35	16.38	1.085	1800	126108	3.250	19.63	99.89
	508.80	6.91	0.101	1200	84072	4.334	11.25	99.99
	276.96	2.05	2.181	3600	252216	6.500	8.55	99.78
MP	1439.10	55.30	33.283	3600	42036	3.318	58.61	96.67
	1094.76	32.00	11.762	3600	84072	3.318	35.32	98.82
	783.35	16.38	26.225	3600	126108	3.318	19.70	97.38
	508.80	6.91	36.325	3600	168144	3.318	10.23	96.37
	276.96	2.05	129.608	3600	252216	3.318	5.37	87.04

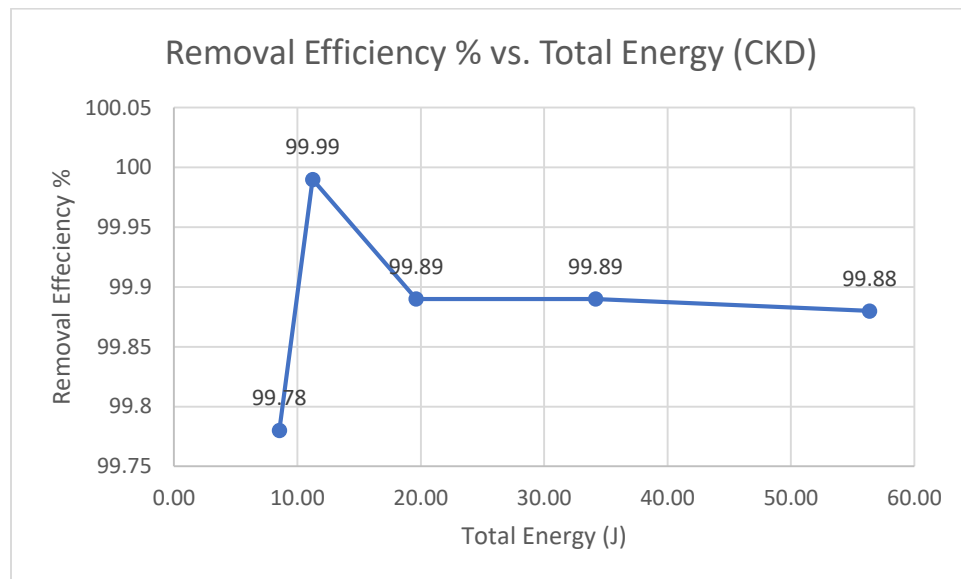


Figure 4.12: Removal Efficiency % vs. Total Energy (CKD)

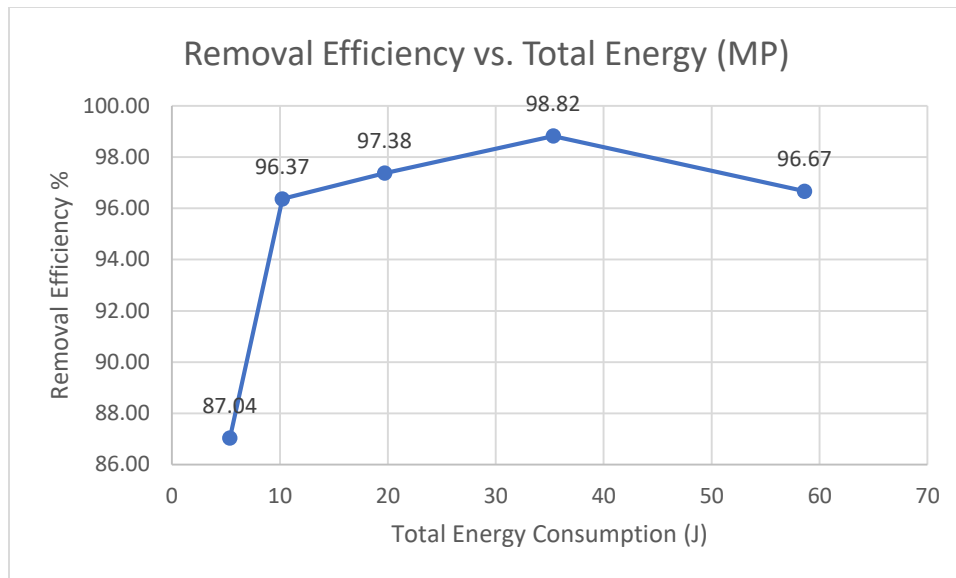


Figure 4.13: Removal Efficiency vs. Total Energy (MP)

#### 4.5 Comparison Between the Performance of Cement bypass kiln dust and Marble Powder in Chromium Removal under different Mixing Conditions

According to Camp, 1995, the rate of particle collisions is directly proportional to the velocity gradient (G) as the increasing in the velocity gradient enhanced the particle collisions and increase the chance to reach the desirable forming rate. However, there is also a relation between the velocity gradient and shear forces; when the velocity gradient increases the shear-forces increase. As a result, excessive speeds lead to excessive shear forces which decreases the flocs formation. This theory can explain the decrease in the removal efficiency after reaching certain value of velocity gradient in both cases of marble powder and cement bypass kiln dust. In addition, both of marble powder and cement bypass kiln dust raise the pH value of the solution above 5 which can be taken as evidence that the removal mechanism of both materials includes chemical precipitation.

Comparing the results of cement bypass kiln dust and marble powder, it can be concluded that cement bypass kiln dust can remove up to 99.99% of Cr III concentration with less total energy and dose than marble powder. Due to this conclusion, cement bypass kiln dust was the elected material to be studied in the rest of the research.

#### 4.6 Effect of CKD dose and Cr III initial concentration

According to the results of phase II, cement bypass kiln dust showed promising results in trivalent chromium removal, so the optimum operation conditions were studied during this phase. In order to study the effects of the CKD dose and the initial concentration of trivalent chromium, jar-test experiments were conducted under the following conditions:

- Flash mixing speed = 150 RPM ( $508.8 \text{ s}^{-1}$ )
- Flocculation mixing speed = 40 RPM ( $70.06 \text{ s}^{-1}$ )
- pH of the solution = 3.00
- Volume of solution = 500 ml
- Temperature = room temperature ( $23^{\circ}\text{C}$ )
- CKD dose = 0.5, 1, 3, 5, 10, 20 (g)
- $\text{Cr}^{3+}$  initial concentration = 500, 1000, 3000, 5000, 6000 (mg/l)

The removal efficiencies were calculated according to results obtained from the experiments and summarized in Table 4–7.



Table 4-7: CKD doses and Cr III initial concentrations results

Cr III initial conc. (mg/l)	CKD Dose (g)	Final Conc. (mg/l)	Initial pH	Final pH	Removal Efficiency %
<b>500</b>	0.5	0.265	3	8.87	99.95
	1	0.000	3	11.57	100
	3	0.000	3	12.40	100
	5	0.000	3	12.56	100
	10	0.000	3	12.74	100
	20	0.000	3	12.77	100
<b>1000</b>	0.5	149.3	3	4.99	85.07
	1	1.058	3	8.75	99.89
	3	0.189	3	11.74	99.98
	5	0.397	3	12.04	99.96
	10	0.811	3	12.33	99.92
	20	0.392	3	12.34	99.96
<b>3000</b>	0.5	2780.9	3	3.81	7.30
	1	2256.7	3	4.20	24.78
	3	28.88	3	5.95	99.04
	5	0.070	3	11.28	100.00
	10	0.000	3	12.28	100.00
	20	0.318	3	12.35	99.99
<b>5000</b>	0.5	5000	3	3.69	0.00
	1	5000	3	3.88	0.00
	3	3107.4	3	4.51	37.85
	5	928.7	3	5.05	81.43
	10	0.961	3	11.28	99.98
	20	1.773	3	12.39	99.96
<b>6000</b>	0.5	5679.8	3	3.50	5.34
	1	5396	3	3.73	10.07
	3	4675.2	3	4.30	22.08
	5	3432	3	4.48	42.80
	10	2.875	3	7.59	99.95
	20	0.437	3	12.29	99.99

Studying the results in Table 4–7 and showed in Figure 4.14, it can be observed that the optimum dose of CKD required to reach the optimum removal efficiency of Cr III increased by increasing the Cr III initial concentration. On the other hand, studying Figure 4.15, it can be observed that the increase in the pH of the solution decreased by increasing the Cr III initial concentration. In addition, the results of this experiment confirmed the observations in the previous phase that the increase in removal efficiency is proportional to the increase in the pH values as shown in Figure 4.16.

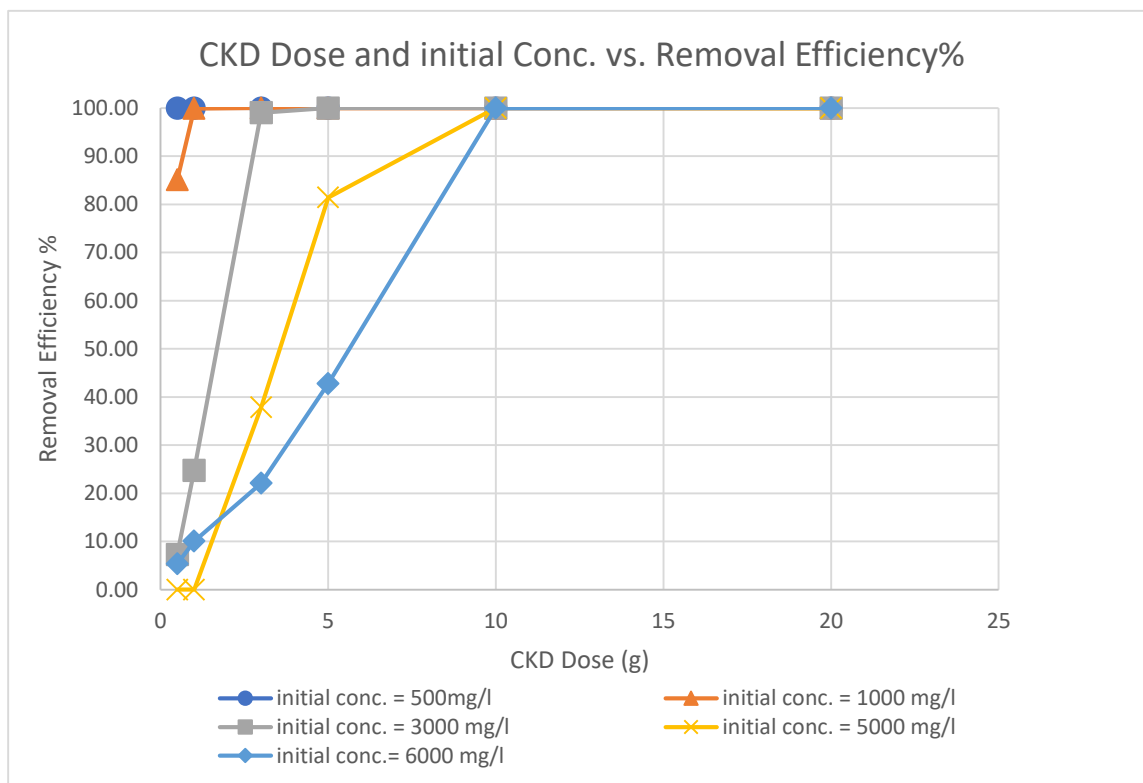


Figure 4.14: CKD Dose and Cr III initial concentration vs. Removal Efficiency (initial pH= 3.00)

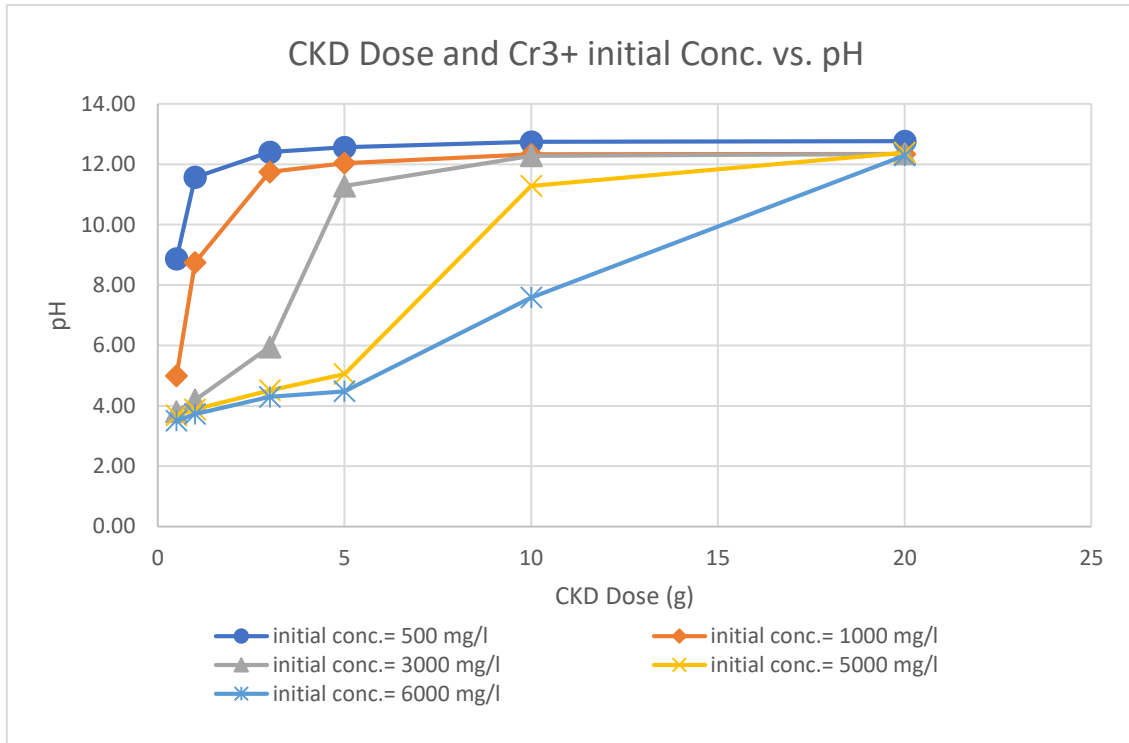


Figure 4.15: CKD Dose and Cr III initial concentration vs. pH (initial pH= 3.00)

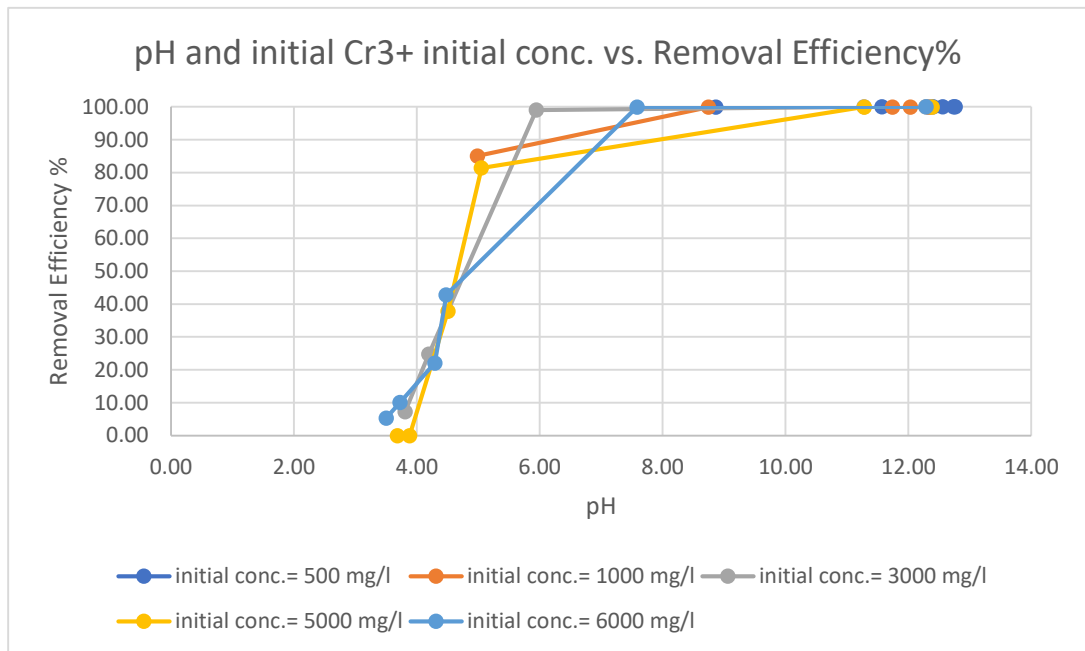


Figure 4.16: pH and Cr III initial concentration vs. Removal Efficiency (initial pH= 3.00)

By increasing the initial concentration of Cr III, the ions of sulfate ( $\text{SO}_4^{2-}$ ) increased and, subsequently, buffering capacity of the solution increased. The increase in buffering capacity increased the resistance of the solution to change the pH value, so the amount of CKD required to increase the pH of the solution increased. Observing that the removal efficiency was proportionally related to the increase in the pH of the solution, the amount of CKD required to reach the optimum removal efficiency increased. According to the graphs, the removal efficiency of CKD reached 100% for all Cr III initial concentrations tested during this phase. Also, it can be noticed that high removal efficiencies were started to show after pH value above 5.0 which can be supported by the fact that expressed by Unceta et al, 2010 that trivalent chromium in pH 4 to 6 tends to form hydroxide products, that is showed as  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}(\text{OH})^{2+}$ , and  $\text{Cr}(\text{OH})_3$  ; then, after pH 6, it precipitates to form only  $\text{Cr}(\text{OH})_3$ .

#### **4.7 Mechanism of Removal of Cement bypass kiln dust**

According to the results discussed in the previous experiment, CKD was acting as a precipitant; so, in order to evaluate the mechanism of CKD, the removal efficiency and performance of CKD were compared to reference precipitants used in tanneries wastewater treatment which are magnesium oxide (MgO) and sodium hydroxide (NaOH).

##### **4.7.1 Cement bypass kiln dust (CKD) and Magnesium Oxide (MgO) Removal Efficiencies**

Jar-test experiments were conducted using MgO as precipitant, with the same doses of CKD used for Cr III removal, under the following conditions:

- Initial  $\text{Cr}^{3+}$  concentration = 1000 mg/l
- pH = 3.00
- Flash mixing speed = 150 RPM ( $462.5 \text{ s}^{-1}$ )
- Flocculation mixing speed = 40 RPM ( $63.7 \text{ s}^{-1}$ )
- Volume of solution = 500 ml
- Temperature = room temperature ( $23^\circ\text{C}$ )

The results obtained from this experiment were compared to the results obtained in case of using CKD under similar conditions as summarized in Table 4–8.

Table 4-8: CKD and MgO Results

Precipitant	Dose (g)	Final Conc. (mg/l)	Initial pH	Final pH	Removal Efficiency %
<b>CKD</b>	0.5	149.3	3	4.99	85.07
	1	1.058	3	8.75	99.89
	3	0.189	3	11.74	99.98
	5	0.397	3	12.04	99.96
	10	0.811	3	12.33	99.92
	20	0.392	3	12.34	99.96
<b>MgO</b>	0.5	127.23	3	5.69	85.07
	1	0.725	3	8.75	99.89
	3	0.161	3	11.71	99.98
	5	0.693	3	12.04	99.96
	10	0.658	3	12.33	99.92
	20	0.341	3	12.34	99.96

According to the results illustrated in fig. Figure 4.17 and the visual observations, both CKD and MgO have the same treatment performance and reached identical removal efficiencies with the same doses. In addition, both materials, as shown in Figure 4.18, raises the pH of the solution to the same values, and the removal efficiencies at these values are identical for both materials. Based on these results, it can be concluded that the performance of CKD in the removal of Cr III matched with the performance of MgO which is a commercial precipitant used in the removal of Cr III from tanneries wastewater.

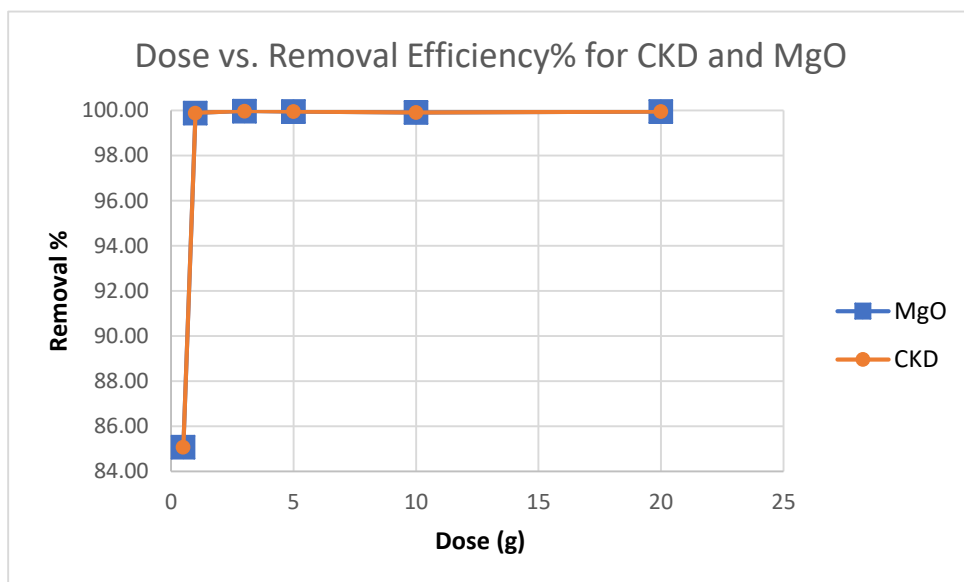


Figure 4.17: Dose vs. Removal Efficiency% for CKD and MgO (initial pH= 3.00)

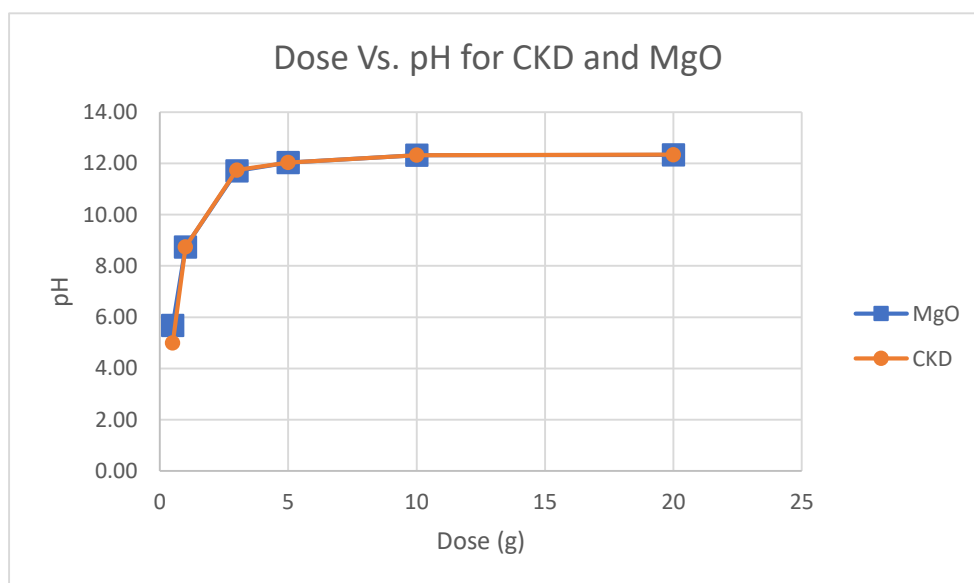


Figure 4.18: Dose vs. pH for CKD and MgO (initial pH= 3.00)

#### 4.7.2 Effect of Increasing pH values Using Cement bypass kiln dust (CKD) and Sodium Hydroxide (NaOH) on the Removal Efficiency

According to the previous discussion, the removal efficiency of Cr III of CKD increased in parallel with the increase in pH values. In order to verify this observation, experiments were conducted using sodium hydroxide solution to compare between the

removal performance of Cr III for CKD and NaOH at the same pH values. The experiments were conducted under the following conditions:

- Initial Cr III concentration = 1000 mg/l
- Flash mixing speed = 150 RPM ( $462.5 \text{ s}^{-1}$ )
- Slow mixing speed = 40 RPM ( $63.7 \text{ s}^{-1}$ )
- Volume of solution = 500 ml
- Temperature = room temperature ( $23^{\circ}\text{C}$ )
- NaOH Solution Molarity = 1M

According to the results obtained from this experiment summarized in Table 4–9 and illustrated in Figure 4.19, the maximum removal efficiency of chromium III using NaOH solution did not exceed 95% which was recorded at pH value 11.74. Comparing the removal efficiencies of CKD and NaOH, it can be observed that there is a huge gap in removal efficiencies. For CKD, the removal efficiency of Cr III reached 85% at pH value 5.2 and the removal efficiency kept increasing till it reached 99.99% at pH 12.33. However, for NaOH, there was no Cr III removal at pH 5.2 and the removal efficiency kept increasing till reaching its maximum value, which was 95%, at pH value of 11.74 after that it started to decrease till reaching 70.53% at pH value of 12.33. According to Esmaeili et al., 2005, increasing the dose of NaOH added leads to excessive increase in pH value causing peptizing resulting in decreasing the removal efficiency as the precipitated chromium starts to dissolve again in the solution. Based on chemical composition of raw CKD provided by the cement factory shown in Table 4–10, it can be observed that CKD is consisting of a composition of chemical materials including two common precipitants, calcium oxide (CaO) and magnesium oxide (MgO), which represented 52.5% and 5.9% of CKD sample, respectively. This composition enhanced the precipitation process and increased the removal efficiency of Cr III.

Table 4-9: CKD and NaOH Results

Material	Material Dose	Initial Conc.	Final Conc.	Initial pH	Final pH	Removal %
NaOH (ml)	2.1	1000	1000	3	5.2	0
	9.4	1000	392.63	3	8.75	60.737
	12.5	1000	49.05	3	11.74	95.095
	15.5	1000	161.05	3	12.04	83.895
	19.6	1000	294.7	3	12.33	70.53
CKD (g)	0.5	1000	149.3	3	5.2	85.07
	1	1000	1.058	3	8.75	99.89
	3	1000	0.189	3	11.74	99.98
	5	1000	0.397	3	12.04	99.96
	10	1000	0.811	3	12.33	99.99

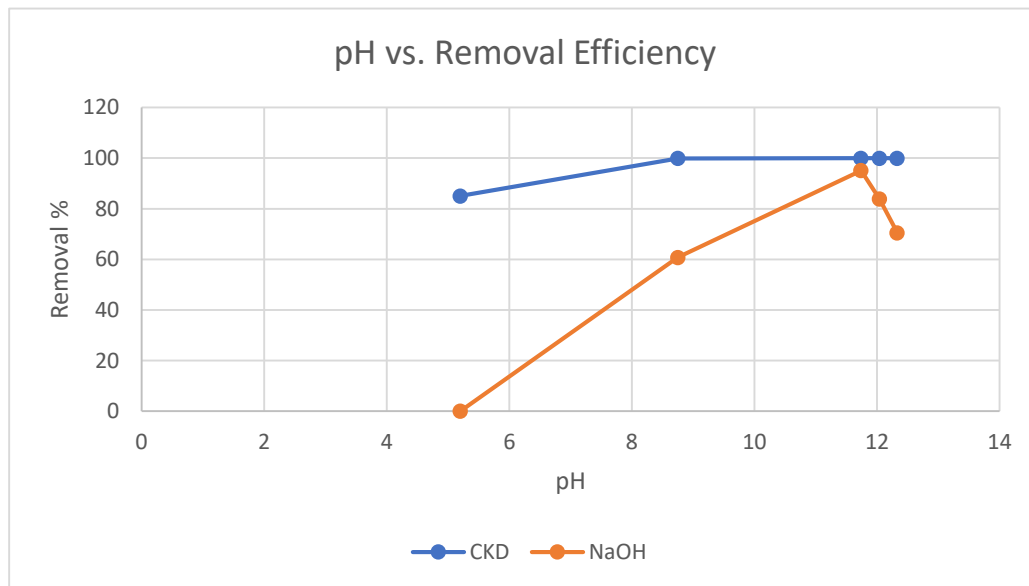


Figure 4.19: pH vs. Removal Efficiency for CKD and NaOH



Table 4–10: Chemical Analysis of CKD

Component	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Cl
%	55.09	3.12	3.33	4.28	16.84	1.15	1.74	3.22	3.428

On the other side, visual observations indicated that, after keeping the solution to settle for 20 min, the precipitated particles stayed suspended in the solution in case of treating using NaOH; however, the precipitated particles settled in the bottom of the beaker creating a grayish green cake layer in case of CKD as shown in Figure 4.20. These observations enhanced the idea that CKD also acts as a coagulant to enhance the settlement process, and improve the treatment performance and removal efficiency of Cr III.

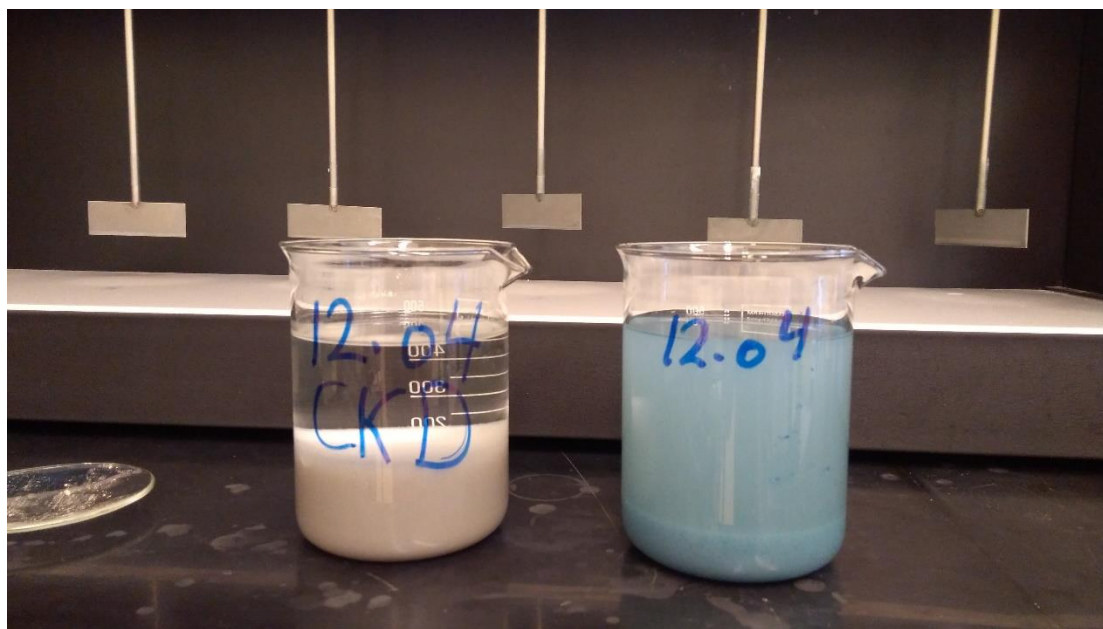


Figure 4.20: Removal of Cr III using CKD (left) and NaOH (right)

#### 4.7.3 General Discussion on Mechanism of Removal

Based on the previous results and discussion, the treatment process using cement bypass kiln dust is based on raising the pH value of the untreated solution which allows Cr III to precipitate as chromium hydroxide ( $\text{Cr}(\text{OH})_3$ ). By studying the results of the chemical analysis of the precipitated sludge, conducted in the Chemistry Administration, summarized in Table 4–11 and illustrated in Figure 4.21, it can be observed that the

percentage of calcium oxide CaO reduced significantly in the precipitated sludge which indicates that the amount of calcium oxide in raw CKD reacted with water to produce calcium hydroxide (slaked lime) according to the following chemical equation:

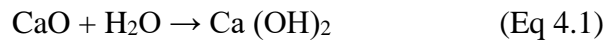


Table 4–11: Chemical Composition of the precipitated sludge (synthetic Solution)

Component	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Insoluble materials	Cr <sup>3+</sup>	Cr <sup>2+</sup>	Cr <sup>6+</sup>
%	12.6	7.4	5.2	0.25	7.9	30.9	28.5	3.2	0.00005

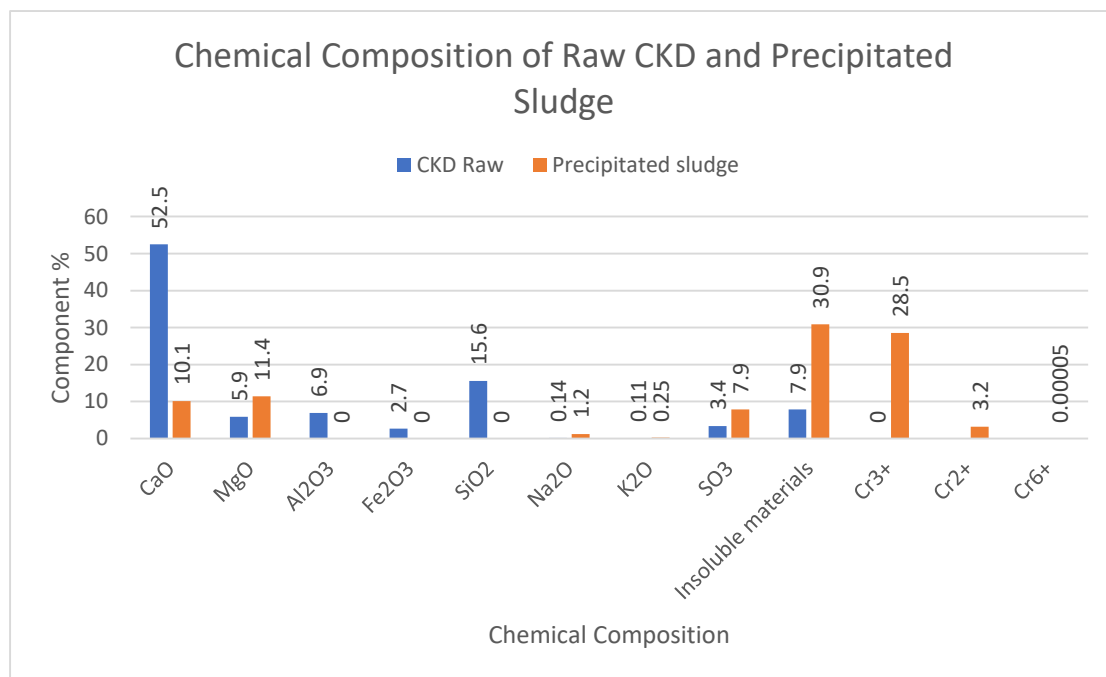


Figure 4.21: Chemical Composition of Raw CKD and precipitated Sludge

The presence of calcium hydroxide increases the OH<sup>-</sup> ions and causing the increase in the pH of the solution. On the other hand, OH<sup>-</sup> ions tends to react with the ions of heavy metals, in this case Cr III, to produce metal hydroxides which are water insoluble; as shown in the following chemical equation:



Combining these results with the visual observations during using sodium hydroxide in Cr III removal, it can be concluded that calcium hydroxide acts also as a coagulant to help the chromium hydroxide particles to combine producing larger flocs and enhance the settling process. So, the removal mechanism of CKD is a combination of chemical precipitation and coagulation processes which gives CKD the ability to reach removal efficiency of 99.99% of Cr III. This excellent treatment performance is similar to the treatment performance of the common precipitant used in the treatment of tanneries wastewater which is magnesium oxide; however, CKD is more economical than magnesium oxide as it is a byproduct from the cement industry which is produced in large quantities.

#### 4.8 The Performance of the Treatment Technique on Real Sample of Tanneries Wastewater

Based on the previous discussion, cement bypass kiln dust showed promising performance in the removal of Cr III from aqueous solution. In phase IV, real tannery wastewater samples were collected from one of the tanneries in Quesna, Monofia Governorate, Egypt. The wastewater samples were collected from the effluent of tanning stage before mixing with the wastewater produced from other stages. The characteristics of the samples were evaluated; however, by analyzing the Cr III concentration, it was found that the concentration was 21,674 mg/l which is more than the highest concentration tested in phase III by around 3.6 times. So, batch experiments were conducted to determine the optimum dose of CKD for the removal of Cr III in this high concentrated wastewater. The results of these experiments were summarized in Table 4–12.

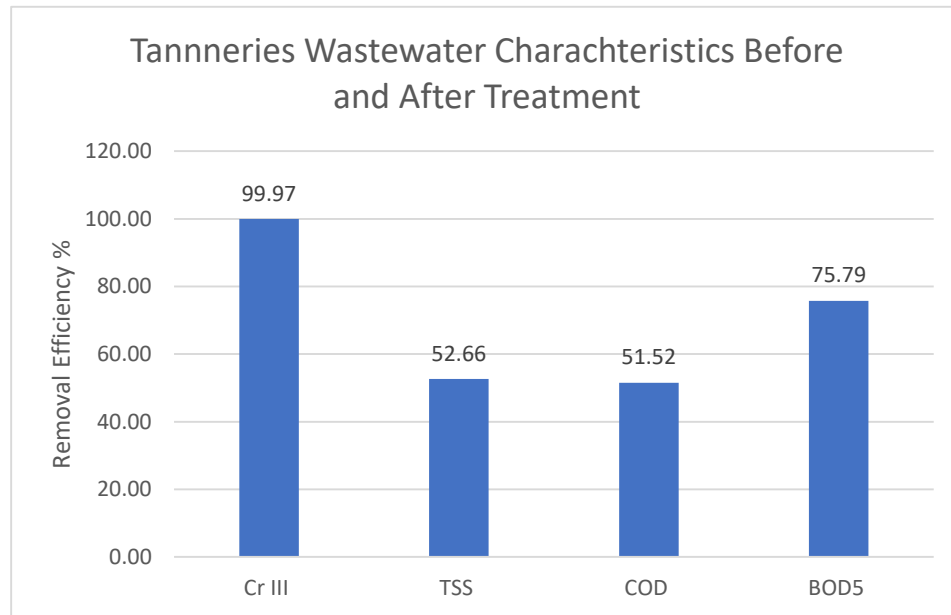
Table 4–12: CKD Doses Tested for Tanneries Wastewater Treatment

CKD dose (g)	Initial Cr <sup>3+</sup> Conc. (mg/l)	Final Cr <sup>3+</sup> Conc. (mg/l)	Initial pH	Final pH	Removal %
10	21674	1520	3.63	7.43	92.99
15	21674	17.608	3.63	8.99	99.92
20	21674	16.543	3.63	8.75	99.92
25	21674	6.584	3.63	9.8	99.97
30	21674	5.148	3.63	10.74	99.98

Based on the results of these experiments, the optimum dose selected to be used in tannery wastewater treatment was 25g/500 ml. The results of treatment were summarized and illustrated in Table 4–13 and Figure 4.22.

*Table 4–13: Effect of CKD Treatment on Tanneries Wastewater Characteristics*

wastewater Characteristics	Before Treatment	After Treatment	Removal Efficiency %
pH	3.63	9.8	-
Cr <sup>3+</sup> Conc. (mg/l)	21,674	6.584	99.97
TSS (mg/l)	395	187	52.66
COD (mg/l)	10500	5090	51.52
BOD <sub>5</sub> (mg/l)	570	138	75.79



*Figure 4.22: Removal Efficiencies of Different Contaminants*

According to the obtained results, CKD showed a very promising performance in tanneries wastewater treatment. The removal efficiency of Cr III reached 99.97% and the chemical oxygen demand (COD) was reduced by 51.52% which can be explained as a result to precipitating Cr III and other chemical elements. Also, the biological oxygen

demand (BOD) was reduced by 75.79% and the total suspended solids (TSS) was reduced by 52.66% which verified that CKD is acting as a coagulant besides its precipitation ability. The coagulation mechanism helped in removing a significant percentage of total suspended solids and biological contaminants. However, it was observed that the volume of precipitated sludge, after 1 h of settling, was 400 ml which represents 80% of the total volume of wastewater used for the treatment. This observation should be taken in consideration when applying this removal technique in conventional unit operations system.

#### **4.9 Efficiency of Chromium Recovery from the Precipitated Sludge Using Sulfuric Acid**

The precipitated sludge, resulted from tanneries wastewater treatment using CKD, was studied before evaluating the chromium recovery process. According to the results obtained from the treatment process, CKD could remove 99.97% of Cr III which became a precipitated sludge. So, using eq. 4.4, chromium III concentration per gram of precipitated sludge is 216.6 mg/g.

$$C = ((C_o - C_f) * V)/m \quad (\text{Eq. 4.3})$$

Where:

C = Cr III concentration per gram of precipitate (mg/g)

C<sub>o</sub> = initial concentration of Cr III in the solution (mg/l)

C<sub>f</sub> = final concentration of Cr III in the supernatant (mg/l)

V = Volume of the solution (l)

m = mass of precipitated sludge (g)

Also, the chemical composition of the precipitated sludge, resulted from tannery wastewater treatment, was analyzed in the Chemistry Administrative and the obtained results were summarized in Table 4–14.

Table 4–14: Chemical Composition of the precipitated sludge (Tannery Wastewater)

Component	Cr <sup>6+</sup>	Cr <sup>3+</sup>	Cr <sup>2+</sup>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Cl <sup>-</sup>
%	0.85	14.6	1.17	12.6	7.4	5.2	0.45	35.6	8.7

In order to evaluate the efficiency of chromium recovery from the precipitated sludge, three factors were studied including reaction time, H<sub>2</sub>SO<sub>4</sub> concentration in the extraction solution and percentage of H<sub>2</sub>SO<sub>4</sub> volume to the weight of the precipitated sludge (v/w). In the following lines, the effect of each of these factors will be discussed.

#### 4.9.1 Effect of Reaction Time in the Chromium Recovery Process

In part I of phase V, experiments were conducted using magnetic stirrer, to evaluate the effect of reaction time on the recovery process, under the following conditions:

- Extraction volume = 514 ml
- H<sub>2</sub>SO<sub>4</sub> concentration = 2.72 %
- Stirring speed = medium speed
- Temperature = room temperature (23°C)

According to the results obtained shown in Table 4–15 and illustrated in Figure 4.23, the recovery efficiency increased by increasing the reaction time. The recovery efficiency increased around 6.5% by increasing the reaction time from 10 to 60 min; however, the increasing rate decreased by increasing the reaction time from 60 to 120 min. The reaction time selected for testing the other two factors was 120 min to guarantee the maximum chromium recovery during the other two series of experiments.

Table 4–15: Phase V results (Part I)

Reaction time (min)	Resulted solution conc. (mg/l)	Cr+3 recovered (mg/g)	% recovered
10	823.6	82.36	38.01
20	851.4	85.14	39.29
40	951.4	95.14	43.91
60	964.7	96.47	44.52
120	1018.6	101.86	47.01

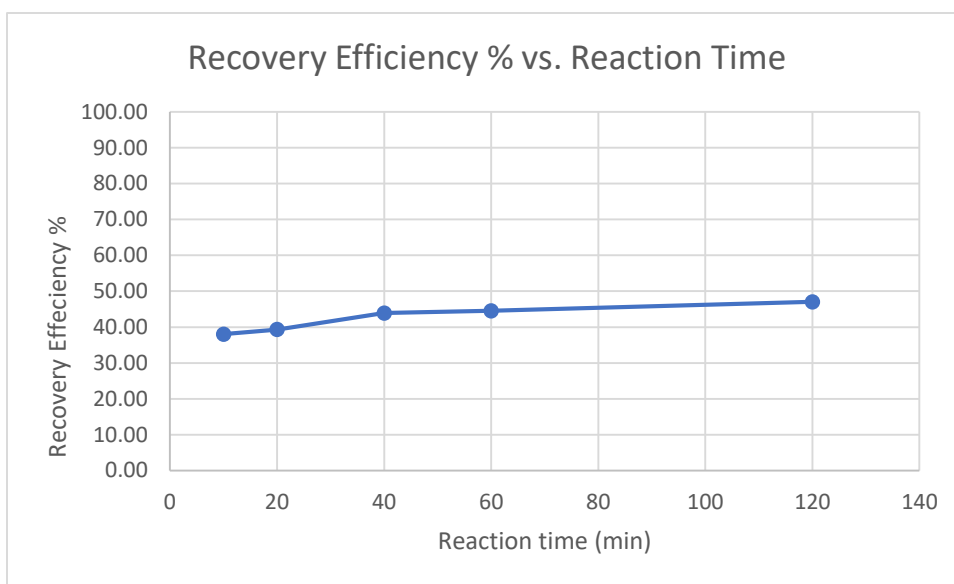


Figure 4.23: Effect of Reaction Time on Recovery Efficiency%

#### 4.9.2 Effect of Sulfuric Acid Concentration on the Chromium Recovery Efficiency

In order to study the effect of  $\text{H}_2\text{SO}_4$  concentration on the chromium recovery efficiency, series of experiments were conducted under the following conditions:

- Reaction time = 120 min
- Stirring speed = medium speed
- Temperature = room temperature (23°C)

The results obtained from these experiments, shown in Table 4–16, indicated that  $\text{H}_2\text{SO}_4$  concentration has a significant effect in the recovery efficiency of Cr III. Studying

Figure 4.24, it can be observed that the recovery efficiency of Cr III increased by increasing  $\text{H}_2\text{SO}_4$  concentration till reaching its maximum recovery efficiency of Cr III at certain  $\text{H}_2\text{SO}_4$  concentration; however, the recovery efficiency decreased by increasing the dose of precipitated sludge due to the increase of Cr III concentration needed to be recovered. As a result, the highest range of recovery efficiency was from 60.3 to 96.1% of Cr III and it was recorder by using precipitated sludge dose of 2.5g which is the lowest dose used in this experiment. On the other hand, the lowest range of recovery efficiency was from 15.7% to 34.3% of Cr III and it was recorded by using precipitated sludge dose of 30 g which is the highest dose used in this experiment. Also, the increase rate in the recovery efficiency due to the increase in  $\text{H}_2\text{SO}_4$  concentration decreased by increasing the sludge dose. Using sludge dose of 2.5 g, the recovery efficiency of Cr III increased by 35.8 % by increasing the  $\text{H}_2\text{SO}_4$  concentration by 6.56 %; however, using sludge dose of 30g, increasing the  $\text{H}_2\text{SO}_4$  concentration by 6.56% increased the recovery efficiency by only 18.6%. According to these interpretations, the maximum recovery efficiency was 96.1% and it was recorded by using  $\text{H}_2\text{SO}_4$  concentration of 7.75% and sludge dose of 2.5g.



Table 4–16: Phase V Results (Phase II)

Experimental Run	Sludge load (g)	H <sub>2</sub> SO <sub>4</sub> Conc. %	Recovered Cr+3 (mg/g)	Recovery Efficiency %
1	2.5	1.19	130.67	60.30
		2.72	119.04	54.93
		5.30	184.69	85.23
		7.75	208.32	96.13
		10.07	173.87	80.24
2	5	1.19	88.76	40.96
		2.72	88.70	40.93
		5.30	93.03	42.93
		7.75	88.96	41.05
		10.07	93.65	43.22
3	10	1.19	81.95	37.82
		2.72	69.44	32.04
		5.30	84.14	38.83
		7.75	80.54	37.17
		10.07	81.32	37.52
4	20	1.19	70.77	32.66
		2.72	76.89	35.48
		5.30	75.21	34.71
		7.75	79.58	36.73
		10.07	74.85	34.54
5	30	1.19	34.11	15.74
		2.72	72.50	33.46
		5.30	69.45	32.05
		7.75	74.42	34.34
		10.07	59.39	27.41

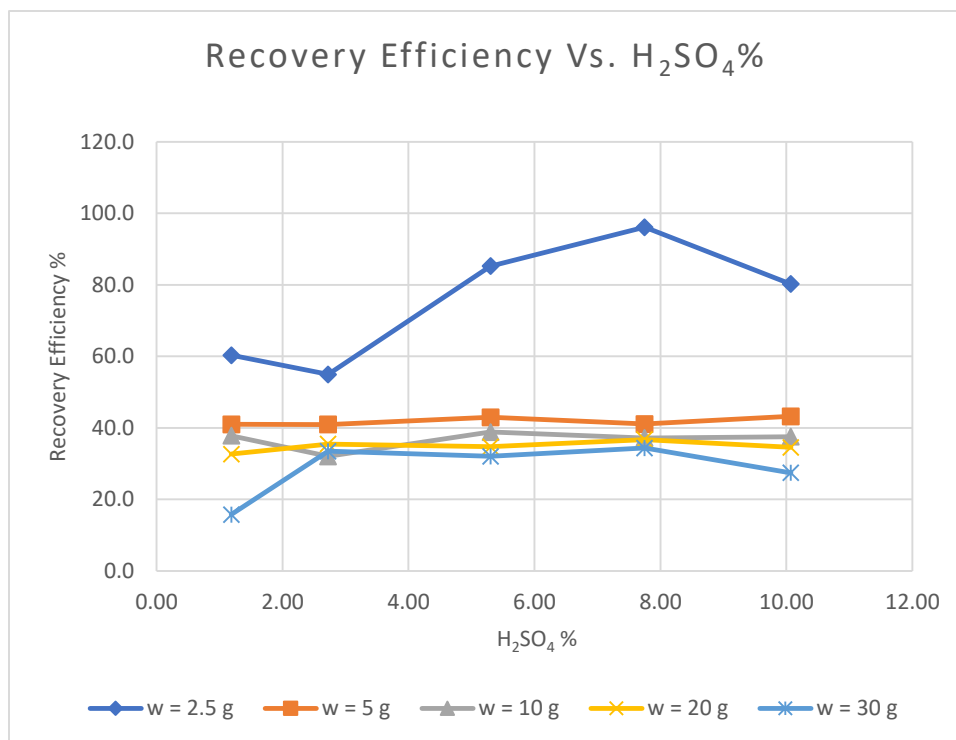


Figure 4.24: H<sub>2</sub>SO<sub>4</sub>% Vs. Recovery Efficiency %

#### 4.9.3 Effect of Percentage of H<sub>2</sub>SO<sub>4</sub> Volume to the Weight of the Sludge on the Recovery Efficiency of Chromium III

In order to evaluate the effect of the percentage of H<sub>2</sub>SO<sub>4</sub> volume to the weight of the sludge closely, series of experiment were conducted over three experimental runs with three different sludge loads included 2.5, 10, and 30 g/500 ml which are the doses resulted in high, medium and low recovery efficiency, respectively. In each experimental run, five different percentages of H<sub>2</sub>SO<sub>4</sub> volume to the weight of the sludge included 0.2, 0.6, 1.4, 5.6 and 11.2 under the following conditions:

- Reaction time = 120 min
- Extraction Volume = 500 or 50 ml
- Stirring speed = medium speed
- Temperature = room temperature (23°C)

The results obtained from the experiments, shown in Table 4–17, confirmed the results obtained from the experiments obtained in the previous part of this phase. As observed in Figure 4.25, the recovery efficiency of Cr III increased by increasing the

percentage of H<sub>2</sub>SO<sub>4</sub> volume to the weight of the sludge (v/w). These results indicated that the recovery efficiency directly proportional to the volume of the concentrated H<sub>2</sub>SO<sub>4</sub> and inversely proportional to the sludge load. Also, it can be observed that the increase in the recovery efficiency was almost constant although the increase in the percentages of H<sub>2</sub>SO<sub>4</sub> volume to the weight of sludge were not constant. The recovery efficiency during the experiments ranged between 24.95 to 45.99 %, which is not a wide range, although the increase in the percentage of H<sub>2</sub>SO<sub>4</sub> volume and sludge load ranged from 3 to 56 times. The maximum recovery efficiency was 45.99% and it was recorded at percentage of H<sub>2</sub>SO<sub>4</sub> volume and the sludge load equal to 11.2 which means that the volume of H<sub>2</sub>SO<sub>4</sub> increased 56 times to raise the recovery efficiency of Cr III by 21% only. This percentage could increase to 96.1% by significantly increase the percentage of H<sub>2</sub>SO<sub>4</sub> volume to the weight of the sludge to be 16.8 with H<sub>2</sub>SO<sub>4</sub> concentration of 7.75% as discussed in the previous section. However, this high percentage resulted in consuming huge amounts of pure water and sulfuric acid to recover chromium from very low amount of precipitated sludge.

*Table 4–17: Phase V Results (Part III)*

volume (H <sub>2</sub> SO <sub>4</sub> )/(weight sludge)	Recovery Efficiency %			Average Recovery Efficiency
	2.5g/500 ml	10g/500ml	30g/500ml	
<b>0.2</b>	22.48	28.49	23.89	24.95
<b>0.6</b>	23.69	32.88	33.45	30.01
<b>1.4</b>	35.10	35.72	35.16	35.33
<b>5.6</b>	45.27	39.87	37.40	40.85
<b>11.2</b>	59.83	47.59	30.56	45.99

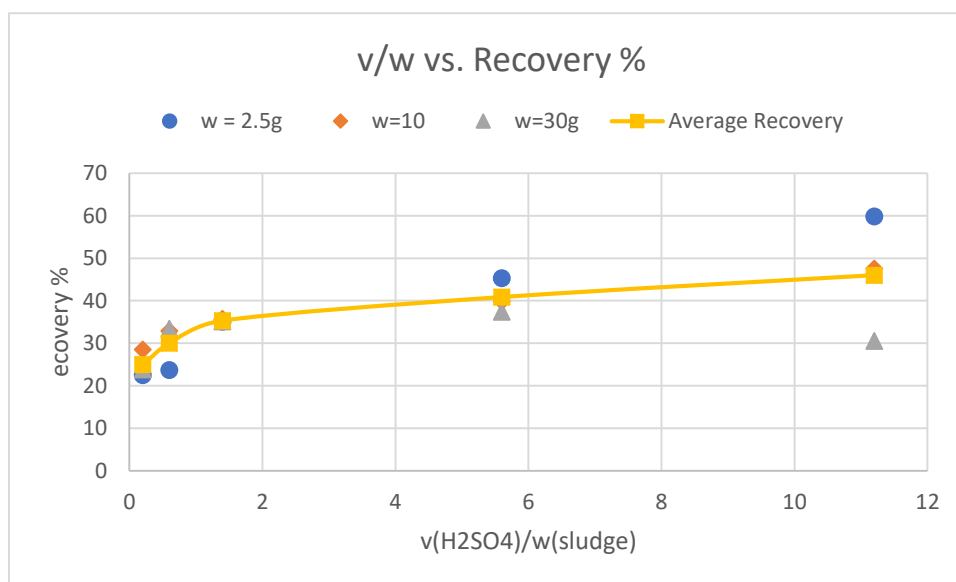


Figure 4.25:  $v(H_2SO_4)/w(sludge)$  vs. Recovery %

Considering the previous discussion, the optimum percentage of  $H_2SO_4$  volume and the sludge load that can be used in Cr III recovery process is 1.4 in which the recovery efficiency recorded 35.33% by increasing the  $H_2SO_4$  volume by only 7 times. In order to increase the recovery efficiency of Cr III,  $H_2SO_4$  concentration of 7.75% would be preferred. That means that 1 liter of extraction solution should be prepared, using 77.5 ml of concentrated  $H_2SO_4$  completed to 1000 ml, in order to recover Cr III from sludge load equal to 55.36 g/l as summarized in Table 4–18.

Table 4–18: Optimum Conditions for chromium III Recovery

Optimum Conditions for Chromium III Recovery	
Total Volume	1000 ml
H <sub>2</sub> SO <sub>4</sub> Conc.	7.75%
Sludge Load	55.36 g/l
Stirring Time	120 min
Stirring Speed	Medium Speed
Temperature	Room Temperature (23°C)

#### 4.9.4 Chemical Composition of the Resulted Sludge from Chromium III Recovery Process and Regeneration

To identify the differences occurred in the resulted sludge from the recovery process of Cr III, 50 g of dry precipitated sludge obtained from the removal process of chromium III were dissolved in 1 liter of extraction solution with H<sub>2</sub>SO<sub>4</sub> concentration of 2.72% to recover chromium III, and the resulted sludge was dried according to the process described in section 3.6.3. The resulted sludge was analyzed, and the results were shown in Table 4–19. The results indicated that the chemical composition of the resulted sludge is different than the chemical composition of raw CKD. Studying Figure 4.26, it can be observed that the percentage of sulfur dioxide (SO<sub>3</sub>) in the resulted sludge reached 54.5%; however, the percentage of sulfur trioxide in the raw cement bypass kiln dust was only 3.22%. The high percentage of sulfur trioxide in the resulted sludge prevents reusing it in the treatment process again. The high percentage of sulfur trioxide increases the acidity of the powder which disables the ability of the powder to increase the alkalinity of the untreated solution to allow Cr III to precipitate.

Table 4–19: Chemical Composition of the Resulted Sludge from the Recovery Process

Component	%
Cr <sup>6+</sup>	0.28
Cr <sup>3+</sup>	6.9
Cr <sup>2+</sup>	0.76
CaO	13.9
MgO	3.6
Na <sub>2</sub> O	0.4
K <sub>2</sub> O	0.15
SO <sub>3</sub>	54.5
Cl <sup>-</sup>	0
Al <sub>2</sub> O <sub>3</sub>	2.7
Fe <sub>2</sub> O <sub>3</sub>	1.2
SiO <sub>2</sub>	13.6

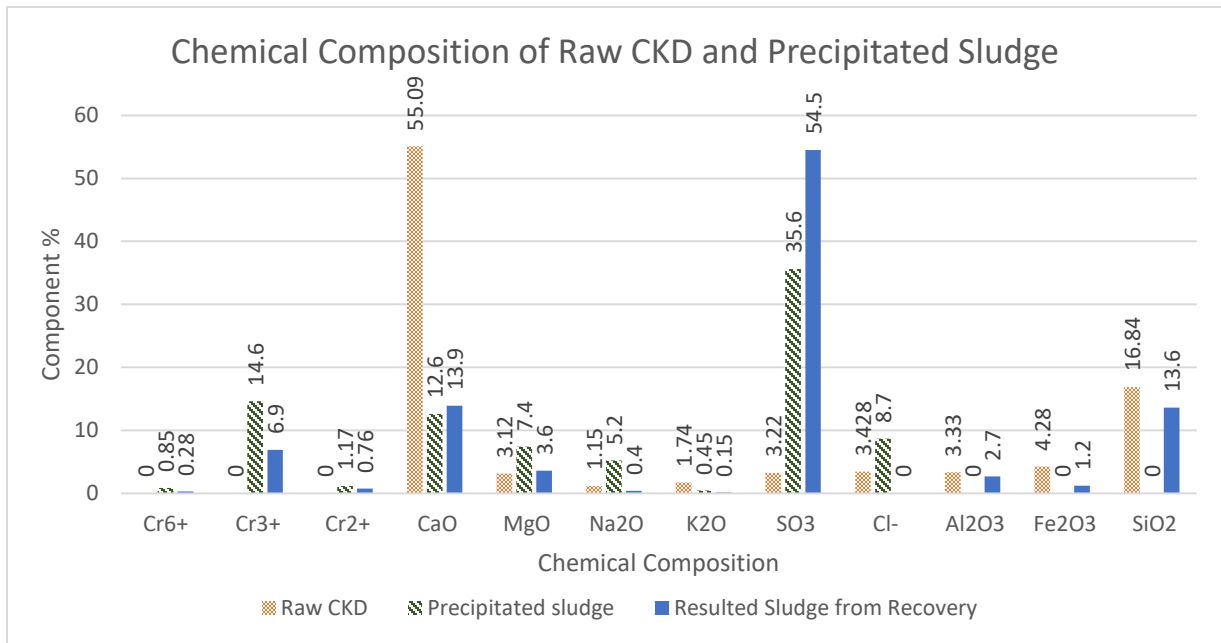


Figure 4.26: Chemical Composition of Raw CKD, Precipitated Sludge and Resulted Sludge from the Recovery

## Chapter 5: Conclusion and Recommendations

### 5.1 Conclusion

Leather tanning is considered as the main process in leather industry and chromium sulfate salt ( $\text{Cr}_2(\text{SO}_4)_3$ ) is the tanning agent used in the chrome tanning process. However, around 30 to 40% of the chromium is discharged as chromium III residues in the tannery's wastewater resulting in serious health and environmental problem in case of discharging to the environment without appropriate treatment. According to these facts, the main objectives of this research is to investigate low cost treatment technique for tanneries wastewater using solid waste materials and evaluate the possibility of recovering chromium III salt from the sludge resulted from the treatment process. To reach these objectives, this study was conducted over five different phases.

In phase I, a comparison was conducted between two groups of solid wastes; the first group contained organic waste materials and the second group contained inorganic waste materials. The results indicated that the inorganic waste materials group, included cement bypass kiln dust and marble powder, showed better performance in chromium III removal than the organic waste materials group included rice husk, rice straw, sugarcane bagasse and sawdust. Cement bypass kiln dust and marble powder raised the alkalinity of the chromium III aqueous solution to pH values of 7.78 and 7.13 which resulted in chromium III removal of 99.9 and 98.8% and forming a layer of precipitated sludge. Based on these results, the inorganic waste materials group was selected for more investigation.

The objective of phase II was to study the effect of mixing conditions on the removal efficiency of chromium III. The studied mixing conditions were the Camp No., which is the multiplication of flocculation mixing speed and flocculation time, and flash mixing speed. According to the results, the removal efficiency of chromium III, for cement bypass kiln dust, increased by decreasing the flash mixing speed and increasing Camp No. (Flocculation mixing speed and flocculation time), till it reached its maximum value of 99.99% at flash mixing speed  $508.8 \text{ s}^{-1}$  (150 RPM), flocculation mixing speed of 40 RPM and flocculation time of 20 min. or Camp No. of 84072, then the efficiency slightly decreased by increasing the flash mixing speed and almost remained constant by increasing

Camp No. However, in the case of marble powder, the removal efficiency of chromium III increased by increasing the flash mixing speed and Camp No., till it reached its maximum value of 98.82 % at flash mixing speed  $1049.76 \text{ s}^{-1}$  (250 RPM), flocculation mixing speed of 30 RPM and flocculation time of 60 min, or Camp No. of 163836, then the efficiency slightly decreased by increasing the flash mixing speed and almost remained constant by increasing Camp No. In addition, it was observed that the increase in the removal efficiency of chromium III was related to the increase in the pH of the solution for both waste materials. Comparing the results according to the energy consumption due to mixing, it can be observed that the energy that cement bypass kiln dust consumed to reach the maximum removal efficiency of chromium III was 11.25 J; on the other hand, the energy that marble powder consumed to reach the maximum removal efficiency of chromium III was 35.32 J. Due to the results of this comparison, cement bypass kiln dust was selected for more investigation.

Phase III of the study was conducted over two parts. Part I was conducted to identify the optimum operation conditions regarding to cement bypass kiln dust dose and initial concentration of chromium III. The obtained results indicated that the maximum removal efficiency of chromium III reached more than 99.9% for all chromium III initial concentrations used; however, the cement bypass kiln dust dose used to reach the maximum removal efficiency increased by increasing chromium III initial concentration. In addition, the results indicated that the pH value of the solution increased by increasing the cement bypass kiln dust dose which indicated that the increase in the removal efficiency of chromium III using cement bypass kiln dust is directly proportional to the increase in the pH value, and the removal efficiency started to exceed 80% after pH value of 5 which agreed with the solubility curve of chromium. According to these results and observations, it was assumed that the removal mechanism of chromium III using cement bypass kiln dust is chemical precipitation.

To study this assumption, the chemical composition of the precipitated sludge was analyzed and compared to the chemical composition of raw cement bypass kiln dust. The results of this comparison indicated that the chemical composition differentiated in both cases; the percentage of chromium III in the precipitated sludge was very higher than the



percentage in raw cement bypass kiln dust. However, the remarkable difference was the significant decrease in the percentage of calcium oxide which indicated that the amount of calcium oxide in raw cement bypass kiln dust reacted with water to produce calcium hydroxide which resulted to increase in  $\text{OH}^-$  ions that tended to react with Cr III ions to form chromium hydroxide solids. In part II, by comparing the treatment performance of cement bypass kiln dust with common precipitant, magnesium oxide, it was concluded that both materials have the same treatment performance and reached identical pH values and removal efficiencies with the same doses. On the other hand, comparing the treatment performance of cement bypass kiln dust and sodium hydroxide, it can be observed that cement bypass kiln dust showed better efficiency for chromium III removal than sodium hydroxide due to the chemical composition of cement bypass kiln dust that contained calcium oxide; in addition, the calcium hydroxide resulted from the reaction of calcium oxide and water acted as a coagulant which enhanced the settlement process and improved the treatment performance.

In phase IV, the treatment technique of using cement bypass kiln dust for chromium III removal was applied on real samples of high concentrated tanneries wastewater, the results indicated that cement bypass kiln dust showed promising treatment performance in which the removal efficiency of chromium III reached 99.97%. In addition, cement bypass kiln dust could reduce the BOD by 75.79%, COD by 51.52% and TSS by 52.66%. However, the volume of the precipitated sludge was 80% of wastewater volume; this observation was considered as a weak point of this technique. Due to the high percentage of volume, this treatment technique requires a good dewatering system to help in handling this high sludge volume.

The precipitated sludge was analyzed, and it was found that chromium III concentration in the precipitated sludge is 216.7 mg/g. In phase V, the efficiency of chromium III recovery was studied using sulfuric acid to reproduce chromium III sulfate that can be used again in tanning process. According to the results, the recovery efficiency increased by increasing the reaction time and sulfuric acid concentration and decreasing the sludge dose. The maximum recovery efficiency was 96.1% and it was recorded by

using extraction solution with sulfuric acid concentration 7.75% and precipitated sludge dose of 2.5g.

## **5.2 Recommendations**

There are several points in this research work that need further investigation, so the recommended research points for future work can include the following:

1. Investigating the efficiency of using cement bypass kiln dust in chromium removal through conventional unit operations system on a pilot scale and studying the economic feasibility of this technique
2. Studying economical methods that can be used for dewatering the high amounts of precipitated sludge resulting from the removal technique.
3. Investigating the technical methods for enhancing the chromium recovery process like using microwave irradiation and studying the economic feasibility of applying it.
4. Investigating the beneficial uses for the precipitated residues resulting from chromium recovery process.

## References

- Abdelhady, S., Borello, D., Shaban, A., & Rispoli, F. (2014). Viability study of biomass power plant fired with rice straw in Egypt. *Energy Procedia*, 61, 211–215. <https://doi.org/10.1016/j.egypro.2014.11.1072>
- Abdulla, H., & Ahmed, E. (2010). Chromium removal from tannery wastewater using chemical and biological techniques aiming zero discharge of pollution, (May).
- Abou-Elela, S. I., Nasr, F. A., Doma, H. S., Ibrahim, H. S., & Badr, N. M. (2005). Sustainable wastewater management in an Egyptian industrial city. *Management of Environmental Quality: An International Journal*, 16(3), 257–266. <https://doi.org/10.1108/14777830510591688>
- Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M. H., Chii, Y. Y., & Siddique, B. M. (2009). Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood. *Desalination*. <https://doi.org/10.1016/j.desal.2009.01.007>
- Ali, O. I. M., Osman, H. H., Sayed, S. A., & Shalabi, M. E. H. (2011). The removal of some rare earth elements from their aqueous solutions on by-pass cement dust (BCD). *Journal of Hazardous Materials*, 195, 62–67. <https://doi.org/10.1016/j.jhazmat.2011.08.014>
- Ali, S. M., Sabae, S. Z., Fayez, M., Monib, M., & Hegazi, N. A. (2011). The influence of agro-industrial effluents on River Nile pollution. *Journal of Advanced Research*, 2(1), 85–95. <https://doi.org/10.1016/j.jare.2010.08.008>
- Aloma, I., Martin-Lara, M. A., Rodriguez, I. L., Zquez, G. B., & Calero, M. (2002). Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse. *Proceedings of the ACM International Multimedia Conference and Exhibition*. <https://doi.org/10.1016/j.jtice.2011.10.011>
- Amer, H. (2015). THE AMERICAN UNIVERSITY IN CAIRO SCHOOL OF SCIENCES AND ENGINEERING REMOVAL OF LEAD FROM INDUSTRIAL WASTEWATER USING A LOW COST WASTE MATERIAL Hayam Ahmed Talaat Amer A thesis submitted in partial fulfillment of the requirements for the degree of Master o, (December).
- Amer, H., El-Gendy, A., & El-Haggar, S. (2017). Removal of lead (II) from aqueous solutions using rice straw. *Water Science and Technology*, 76(5), 1011–1021. <https://doi.org/10.2166/wst.2017.249>
- Asif, Z., & Chen, Z. (2017). Removal of arsenic from drinking water using rice husk. *Applied Water Science*, 7(3), 1449–1458. <https://doi.org/10.1007/s13201-015-0323-x>
- Ayaliew Werkneh, A., Hayelom Dargo, A., & Ayalew, A. (2014). *Tannery Waste Water Treatment: A Review. International Journal of Emerging Trends in Science and Technology*. Retrieved from [www.ijetst.in](http://www.ijetst.in)
- C.R.Ramakrishnaiah, & Prathima, B. (2012). *HEXAVALENT CHROMIUM REMOVAL*

- Camp, T. R. (1955). *Flocculation and Flocculation Basins*. American Society of Civil Engineers.
- Cetin, G., Kocaoba, S., & Akcin, G. (2013). Removal and recovery of chromium from solutions simulating tannery wastewater by strong acid cation exchanger. *Journal of Chemistry*, 2013(Iii). <https://doi.org/10.1155/2013/158167>
- Ding, Y., Jing, D., Gong, H., Zhou, L., & Yang, X. (2012). Biosorption of aquatic cadmium(II) by unmodified rice straw. *Bioresource Technology*. <https://doi.org/10.1016/j.biortech.2012.01.110>
- Dixit, S., Yadav, A., Dwivedi, P. D., & Das, M. (2015). Toxic hazards of leather industry and technologies to combat threat: A review. *Journal of Cleaner Production*, 87(C), 39–49. <https://doi.org/10.1016/j.jclepro.2014.10.017>
- Egypt Today. (2019). Industrial sector weighs up to 20% of growth rate: Min. Retrieved August 12, 2019, from <https://www.egypttoday.com/Article/3/66870/Industrial-sector-weighs-up-to-20-of-growth-rate-Min>
- El-Khateeb, M. A., Nashy, E.-S. H. A., Ghany, N. A. A., & Awad, A. M. (2017). Environmental impact elimination of chrome tanning effluent using electrocoagulation process assisted by chemical oxidation. *Desalination and Water Treatment*, 65(March), 147–152. <https://doi.org/10.5004/dwt.2017.20250>
- El-Sabbagh, S., & Mohamed, O. (2010). Recycling of Chrome-Tanned Leather Waste in Acrylonitrile Butadiene Rubber. *Applied Polymer Science*, 116(5), 2658–2667. <https://doi.org/10.1002/app>
- Elabbas, S., Mandi, L., Berrekhis, F., Pons, M. N., Leclerc, J. P., & Ouazzani, N. (2016). Removal of Cr(III) from chrome tanning wastewater by adsorption using two natural carbonaceous materials: Eggshell and powdered marble. *Journal of Environmental Management*, 166, 589–595. <https://doi.org/10.1016/j.jenvman.2015.11.012>
- Elnaggar, A., Leona, M., Nevin, A., & Heywood, A. (2017). The Characterization of Vegetable Tannins and Colouring Agents in Ancient Egyptian Leather from the Collection of the Metropolitan Museum of Art. *Archaeometry*, 59(1), 133–147. <https://doi.org/10.1111/arc.12239>
- EPA, U. S. E. P. A. (2000). Wastewater Technology Fact Sheet Chemical Precipitation. *Office of Water Washington, D.C.*
- Esmaili, A., Mesdaghi nia, A., & Vazirinejad, R. (2005). Chromium ( III ) Removal and Recovery from Tannery Wastewater by Precipitation Process. *American Sciences, Applied Publications, Science*, 2(1546–9239), 1471–1473.
- Fahim, N. F., Barsoum, B. N., Eid, A. E., & Khalil, M. S. (2006). Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste. *Journal of Hazardous Materials*, 136(2), 303–309.

<https://doi.org/10.1016/j.jhazmat.2005.12.014>

- Gautam, R. K., Sharma, S. K., Mahiya, S., & Chattopadhyaya, M. C. (2014). CHAPTER 1. Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation. *Heavy Metals In Water*, (October), 1–24. <https://doi.org/10.1039/9781782620174-00001>
- Ghazy, S E, Samra, S. E., Mahdy, A. M., & El-Morsy, S. M. (2003). Removal of Copper(II) Ions from Aqueous Solutions. I. Adsorption Studies Using Powdered Marble Wastes as Sorbent. *Adsorption Science & Technology*, 21.
- Ghazy, Shaban E., & Gad, A. H. M. (2008). Separation of Zn(II) by sorption onto powdered marble wastes. *Indian Journal of Chemical Technology*, 15, 433–442. <https://doi.org/10.1016/j.arabjc.2010.10.031>
- Glavič, P., & Bogataj, M. (2011). Water Networks – Theory and Practice. *Security of Industrial Water Supply and Management NATO Science for Peace and Security Series C: Environmental Security*, (10.1007/978-94-007-1805-0\_2), 13–30.
- Grassi, M., Kaykioglu, G., & Belgiorno, V. (2012). Emerging Compounds Removal from Wastewater, 15–37. <https://doi.org/10.1007/978-94-007-3916-1>
- Guo, Z. R., Zhang, G., Fang, J., & Dou, X. (2006). Enhanced chromium recovery from tanning wastewater. *Journal of Cleaner Production*. <https://doi.org/10.1016/j.jclepro.2005.01.005>
- Gupta, S., & Babu, B. V. (2009). Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: Equilibrium, kinetics and regeneration studies. *Chemical Engineering Journal*. <https://doi.org/10.1016/j.cej.2009.01.013>
- HADDAD, S. S. G. (2018). The Status of Leather Supply Chain in Egypt: an Exploratory Study for the INNOLEA Project, 105–110. <https://doi.org/10.24264/icams-2018.i.15>
- Hintermeyer, B. H., & Tavani, E. L. (2017). Chromium(III) recovery from tanning wastewater by adsorption on activated carbon and elution with sulfuric acid. *Environmental Engineering Research*, 22, 149–156. <https://doi.org/10.4491/eer.2016.070>
- Homagai, P. L., Ghimire, K. N., & Inoue, K. (2010). Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse. *Bioresource Technology*. <https://doi.org/10.1016/j.biortech.2009.11.073>
- Ibrahim, M. I. M., & Mohamed, N. A. E. M. (2016). Towards Sustainable Management of Solid Waste in Egypt. *Procedia Environmental Sciences*, 34, 336–347. <https://doi.org/10.1016/j.proenv.2016.04.030>
- Itodo, A., Khan, M., & Feka, D. (2018). Tannery Wastewater Evaluation and Remediation: Adsorption of Trivalent Chromium Using Commercial and Regenerated Adsorbents. *Journal of Water Technology and Treatment Methods*, 1(1), 1–8. <https://doi.org/10.31021/jwt.20181105>
- Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014).

- Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7(2), 60–72. <https://doi.org/10.2478/intox-2014-0009>
- Khan, S. A., Ibrahim, M., Jamil, Y., Islam, M. S., & Abbas, F. (2013). Spectrochemical analysis of soil around leather tanning industry using laser induced breakdown spectroscopy. *Journal of Chemistry*, 2013. <https://doi.org/10.1155/2013/894020>
- Kocaoba, S., & Akcin, G. (2002). Removal and recovery of chromium and chromium speciation with MINTEQA2. *Talanta*, 57(1), 23–30. [https://doi.org/10.1016/S0039-9140\(01\)00677-4](https://doi.org/10.1016/S0039-9140(01)00677-4)
- Kocurek, P., Kolomazník, K., & Barinova, M. (2015). Removal of chromium from wastewater by reverse osmosis. *Russian Journal of Physical Chemistry A*, 89(7), 1238–1243. <https://doi.org/10.1134/s0036024415070055>
- Kolomaznik, K., Adamek, M., Andel, I., & Uhlirova, M. (2008). Leather waste-Potential threat to human health, and a new technology of its treatment. *Journal of Hazardous Materials*, 160(2–3), 514–520. <https://doi.org/10.1016/j.jhazmat.2008.03.070>
- Kumar, P. S., Kirthika, K., & Kumar, K. S. (2008). Removal of Hexavalent Chromium Ions from Aqueous Solutions by an Anion-Exchange Resin. *Adsorption Science & Technology*, 26(9), 693–703. <https://doi.org/10.1260/026361708788251402>
- Kumar, U., & Bandyopadhyay, M. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology*, 97(1), 104–109. <https://doi.org/10.1016/j.biortech.2005.02.027>
- Louarrat, M. (2018). Removal of Chromium Cr(VI) of Tanning Effluent with Activated Carbon from Tannery Solid Wastes. *American Journal of Physical Chemistry*, 6(6), 103. <https://doi.org/10.11648/j.ajpc.20170606.11>
- Ludvik, J. (2000). *Regional Programme for Pollution Control in the Tanning Industry in South-East Asia THE SCOPE FOR DECREASING POLLUTION LOAD IN LEATHER PROCESSING Prepared by J. Ludvík UNIDO Consultant in Leather Pollution Control.*
- Mackie, A. L., & Walsh, M. E. (2012). Bench-scale study of active mine water treatment using cement kiln dust (CKD) as a neutralization agent. *Water Research*. <https://doi.org/10.1016/j.watres.2011.10.030>
- Maher, M., & El-Khair, A. (2010). *PACT II PROGRAMME INTRA-REGIONAL TRADE COMPONENT PROMOTING INTERNATIONAL AND INTRA-AFRICAN TRADE IN LEATHER SUPPLY / DEMAND SURVEY EGYPT.*
- Mahmood-ul-Hassan, M., Suthar, V., Rafique, E., Ahmad, R., & Yasin, M. (2015). Kinetics of cadmium, chromium, and lead sorption onto chemically modified sugarcane bagasse and wheat straw. *Environmental Monitoring and Assessment*. <https://doi.org/10.1007/s10661-015-4692-2>
- Malik, D. S., Jain, C. K., & Yadav, A. K. (2016). Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review. *Applied Water Science*. <https://doi.org/10.1007/s13201-016-0401-8>

- Martín-Lara, M. Á., Rico, I. L. R., Vicente, I. de la C. A., García, G. B., & de Hoces, M. C. (2010). Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions. *Desalination*. <https://doi.org/10.1016/j.desal.2010.02.015>
- Mary Lissy, P. N., & Madhu, D. G. (2010). Removal of Heavy Metals from Waste Water Using Water Hyacinth. *Proc. of Int. Conf. on Advances in Civil Engineering 2010*, (January), 42–47.
- Meshram, P., Sahu, S. K., Pandey, B. D., Kumar, V., & Mankhand, T. R. (2012). Removal of Chromium(III) from the Waste Solution of an Indian Tannery by Amberlite IR 120 Resin. *International Journal of Nonferrous Metallurgy*, 01(03), 32–41. <https://doi.org/10.4236/ijnm.2012.13005>
- Minas, F., Chandravanshi, B. S., & Leta, S. (2017). Chemical precipitation method for chromium removal and its recovery from tannery wastewater in Ethiopia. *Chemistry International*, 3(4), 291–305.
- MOELLER, D. W. (2019). *Solid Waste. Environmental Health, Third Edition*. <https://doi.org/10.2307/j.ctvjz80w7.13>
- Mohammed, K., & Sahu, O. (2019). Recovery of chromium from tannery industry waste water by membrane separation technology: Health and engineering aspects. *Scientific African*, 4, e00096. <https://doi.org/10.1016/j.sciaf.2019.e00096>
- Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents-A critical review. *Journal of Hazardous Materials*, 142(1–2), 1–53. <https://doi.org/10.1016/j.jhazmat.2007.01.006>
- Monayeri, D. S., Monayeri, O. D., Gohary, E. H., & Aboul-Fotoh, A. M. (2011). Industrial Wastewater Treatment Systems in Egypt: Difficulties and Proposed Solutions. *Security of Industrial Water Supply and Management NATO Science for Peace and Security Series C: Environmental Security*, (978-94-007-1805-0), 209–230.
- Mostafa, H. M., Rashed, M., & Mostafa, A. H. (2005). UTILIZATION OF BY-PASS KILN DUST FOR TREATMENT OF TANNERIES EFFLUENT WASTEWATER. Sharm El-Sheikh, Egypt: Ninth International Water Technology Conference, IWTC9 2005.
- Nashy, E., & Eid, K. A. (2018). Reduction of Chrome Tanning Effluent Impact and Enhancement of Leather Properties Based on High Exhaustion of Chrome Tan. *Egyptian Journal of Chemistry*, 0(0), 0–0. <https://doi.org/10.21608/ejchem.2018.4393.1387>
- Nazer, D. W., Al-Sa'Ed, R. M., & Siebel, M. A. (2006). Reducing the environmental impact of the unhairing-liming process in the leather tanning industry. *Journal of Cleaner Production*, 14(1), 65–74. <https://doi.org/10.1016/j.jclepro.2005.04.002>
- New Hampshire Department of Environmental Services. (2009). Ion Exchange Treatment of Drinking Water. *Cycle*.
- Oliveira, H. (2012). Chromium as an Environmental Pollutant: Insights on Induced Plant

- Toxicity. *Journal of Botany*, 2012, 1–8. <https://doi.org/10.1155/2012/375843>
- Organization(UNIDO), U. N. I. D. (2011). *INTRODUCTION TO TREATMENT OF TANNERY EFFLUENTS*.
- Ouafi, R., Rais, Z., Taleb, M., & Asri, M. (2017). Sawdust in the treatment of heavy metals-contaminated wastewater, (October 2018). Retrieved from <https://www.researchgate.net/publication/321680452>
- Pansward, T., Chavalparit, O., Chandung, C., & Anotai, J. (2001). Economic considerations of chromium recovery from. *Waste Management & Research*, 19(0734-242X), 450–455.
- Patel, J. (2016). Ion exchange resins, (July), 0–7.
- Ramanujam, R. A., Ganesh, R., & Kandasamy, J. (2010). WASTEWATER TREATMENT TECHNOLOGY FOR TANNING SA NE M SC PL O E – C EO AP LS TE S M SC PL O E – C EO. *Encyclopedia of Life Support Systems (EOLSS)*.
- Reynolds, T., & Richard, P. (1996). *1995\_UnitOperationsandProcessesinEnvironmentalEngineering\_SecondEdition.pdf*.
- Rocha, C. G., Zaia, D. A. M., Alfaya, R. V. da S., & Alfaya, A. A. da S. (2009). Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents. *Journal of Hazardous Materials*. <https://doi.org/10.1016/j.jhazmat.2008.11.074>
- Rodríguez, M. C., Barsanti, L., Passarelli, V., Evangelista, V., Conforti, V., & Gualtieri, P. (2007). Effects of chromium on photosynthetic and photoreceptive apparatus of the alga *Chlamydomonas reinhardtii*. *Environmental Research*, 105(2), 234–239. <https://doi.org/10.1016/j.envres.2007.01.011>
- Sabumon, P. (2017). Perspectives on Biological Treatment of Tannery Effluent. *OMICS International*, 2(2). <https://doi.org/10.4172/2475-7675.1000128>
- Sadegh, H., & Ali, G. A. M. (2018). Potential Applications of Nanomaterials in Wastewater Treatment, (June), 51–61. <https://doi.org/10.4018/978-1-5225-5754-8.ch004>
- Sánchez-Martín, J., Beltrán-Heredia, J., & Peres, J. A. (2012). Improvement of the flocculation process in water treatment by using *Moringa oleifera* seeds extract. *Brazilian Journal of Chemical Engineering*, 29(3), 495–501. <https://doi.org/10.1590/S0104-66322012000300006>
- Shi, T., Wang, Z., Liu, Y., Jia, S., & Changming, D. (2009). Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins. *Journal of Hazardous Materials*, 161(2–3), 900–906. <https://doi.org/10.1016/j.jhazmat.2008.04.041>
- Sobhanardakani, S., Parvizimosaed, H., & Olyaie, E. (2013). Heavy metals removal from wastewaters using organic solid waste—rice husk. *Environmental Science and Pollution Research*, 20(8), 5265–5271.



- Stearns, D. M., Belbruno, J. J., & Wetterhahn, K. E. (2018). A prediction of chromium(III) accumulation in humans from chromium dietary supplements. *The FASEB Journal*, 9(15), 1650–1657. <https://doi.org/10.1096/fasebj.9.15.8529846>
- Tripathi, A., & Dwivedi, A. K. (2012). Studies on Recovery of Chromium From Tannery, 28(1).
- Unceta, N., Séby, F., Malherbe, J., & Donard, O. F. X. (2010). Chromium speciation in solid matrices and regulation: A review. *Analytical and Bioanalytical Chemistry*, 397(3), 1097–1111. <https://doi.org/10.1007/s00216-009-3417-1>
- UNEP. (1996). *Cleaner production in leather tanning*.
- Wang, L., Hung, Y.-T., & Shammas, N. (2005). *physiochemical treatment processes*. New Jersey: Human Press.
- Wang, Y. (2019). Release of Chrome in Chrome Tanning and Post Tanning Processes, (July 2012).
- WWAP (United Nations World Water Assessment Programme). (2018). *NATURE-BASED SOLUTIONS FOR WATER World Water Assessment Programme United Nations Educational, Scientific and Cultural Organization Sustainable Development Goals water and sanitation ter ent e Sustainable Development Goals water and sanitation*. Retrieved from [www.unesco.org/open-access/](http://www.unesco.org/open-access/)
- Yasemin, B., & Zeki, T. (2006). *Removal of heavy metals from aqueous solution by sawdust adsorption*. Retrieved from [www.jesc.ac.cn](http://www.jesc.ac.cn)
- Zaki, N. G., Khattab, I. A., & Abd El-Monem, N. M. (2007). Removal of some heavy metals by CKD leachate. *Journal of Hazardous Materials*, 147(1–2), 21–27. <https://doi.org/10.1016/j.jhazmat.2006.12.057>
- Zaki, T., Kafafi, A.-G., Mina, M. B., Abd-El-Halim, A.-E.-H. M., & Saber, M. (2013). Annual Report for Solid Waste Management in Egypt, 2013, 1–162. Retrieved from [http://cairoclimatetalks.net/sites/default/files/EN Annual Report on Waste in Egypt\\_2013.pdf](http://cairoclimatetalks.net/sites/default/files/EN%20Annual%20Report%20on%20Waste%20in%20Egypt_2013.pdf)

# Appendix

Ministry of Trade & Industry  
Chemistry Administration  
Established in 1898



وزارة التجارة والصناعة  
مصلحة الكيمياء  
تأسست عام ١٨٩٨ م

الإدارة المركزية لمعامل القاهرة  
الإدارة العامة لمعامل الإشتاتية

المعمل المختص/ مواد البناء

تقرير الاختبار (Test Report)

بيانات العينة

كود/ شهادة الوارد للعينة: ٢٠١٩/٤٣٥/٠١١

كود المعمل الرئيسي: ٢٠١٩/٤٣٥/٠١١

مسمى العينة: راسب من إعادة الكروم

تاريخ ورود العينة: ٢٠١٩/٤/١٠

عدد الصفحات/ العدد الكلي: (١/١)

كود المعمل الفرعي:

وصف العينة: بودرة رمادية اللون

تاريخ إصدار التقرير: ٢٠١٩/٥/٩

مطالب العميل

الفحص المطلوب: تحليل كيميائي كامل - نسبة الكروم -

المواصفة القياسية:

بيانات العميل

اسم العميل: أ / سارة إيهاب عبد القادر

جهة العميل:

نتائج الاختبارات

الاختبارات الكيميائية ( الوحدة )	النسبة (%)	النتيجة
الكروم سداسي الذائب في الماء (Cr <sup>+6</sup> )	( % )	٠,٢٨
الكروم الثلاثي (Cr <sup>+3</sup> )	( % )	٦,٩
الكروم الثنائي (Cr <sup>+2</sup> )	( % )	٠,٧٦
أكسيد الكالسيوم (CaO)	( % )	١٣,٩
أكسيد الماغنسيوم (MgO)	( % )	٣,٦
أكسيد الصوديوم (Na <sub>2</sub> O)	( % )	٠,٤
أكسيد البوتاسيوم (K <sub>2</sub> O)	( % )	٠,١٥
ثالث أكسيد الكبريت (SO <sub>3</sub> )	( % )	٥٤,٥
أكسيد الألومنيوم (Al <sub>2</sub> O <sub>3</sub> )	( % )	٢,٧
أكسيد الحديدك (Fe <sub>2</sub> O <sub>3</sub> )	( % )	١,٢
ثاني أكسيد السيليكون (SiO <sub>2</sub> )	( % )	١٣,٦

- هذه النتيجة تخص العينة المقدمة ولا تمثل إلا الكمية الممثلة منها العينة ، وتمثيلها لأي كميات أخرى هي مسئولية جهة سحب العينة.

- يحتفظ ببقايا العينات بعد اختبارها بمعامل المصلحة لمدة أقصاها شهر من تاريخ الإختبار .

- سريان العمل بتقرير الاختبار لمدة ثلاثة أشهر للعينات الغذائية ولمدة ستة شهور لباقي العينات من تاريخ إصدار التقرير . ( نهاية التقرير )

مدير الإدارة

المدير العام

رئيس الإدارة المركزية لمعامل القاهرة

محرر التقرير: راضي

الختم:

تقرير الاختبار يطبع تحت مسئولية مصلحة الكيمياء فقط

٤ ١٩ ٥ ١٢



الإدارة المركزية لمعامل القمار

الإدارة العامة لمعامل (شركة)

معمل المختص مواد البناء

تقرير الاختبار (Test Report)

بيانات العينة

عدد الصفحات العدد الكلي: (١/١)

كود المعمل الفرعي:

وصف العينة: مادة رابطة الاسفلت

تاريخ إصدار التقرير: ٢٠١٩/٥/٩

كود شهادة التوريد للعينة

كود المعمل الرئيسي: ٢٠١٩/٥٣٤/١٠١

اسم العينة: راسب من ماء لادعة

تاريخ ورود العينة: ٢٠١٩/٥/١٠

مطالب العينة

الحصول المطلوب: تحليل كيميائي كامل - نسبة الكبريت

الموصوفة الكيميائية:

بيانات العميل

جهة العميل:

اسم العميل: شركة يهت عند القادر

نتائج الاختبارات

الاختبارات الكيميائية (الوحدة)

النتيجة

٠,٨٥

(%)

١٤,٦

(%)

١,١١

(%)

١٢,٦

(%)

٧,٤

(%)

٨,١

(%)

٥,٢

(%)

٠,٤٥

(%)

٣٥,٦

(%)

٤,٧

(%)

الكبريت المشافي الثالث في الماء (Cr<sup>٥+</sup>)

كبريت ثنائي (Cr<sup>٣+</sup>)

كبريت ثنائي (Cr<sup>٢+</sup>)

أكسيد الكالسيوم (CaO)

أكسيد المغنسيوم (MgO)

الكبريتات على صورة (Cl)

أكسيد الصوديوم (Na<sub>2</sub>O)

أكسيد البوتاسيوم (K<sub>2</sub>O)

ثلاث أكسيد الكبريت (SO<sub>3</sub>)

الرقمية عند درجة ٥٠°م

- هذه نتيجة فحص العينة المقدمة ولا يمثل إلا الكمية الممتلئة منها العينة، وبمضيها لأي كميات أخرى في مسئولية جهة سحب العينة.

- يحفظ بقايا العينات بعد اختبارها بمعمل المصلحة لمدة أقصاها شهر من تاريخ الإحصار.

- سريان العمل بتقرير الإحصار لمدة ثلاثة أشهر للعينات العذائية ولمدة سنة للباقي العينات من تاريخ إصدار التقرير. (نهاية التقرير)

المدير العام

مدير الإدارة

(  
٢٠١٩  
رئيس الإدارة المركزية لمعامل القاهرة

(  
م/كريم غمارس

الختم:

(  
خلفه  
محرر التقرير: راسب  
٢٠١٩/٥/٩

٤٦١٩  
تقرير الاختبار بطبق تحت مسئولية مصلحة الكيمياء فقط  
١٩ ١٢



الإدارة المركزية لمعامل / القاهرة  
الإدارة العامة لمعامل / الإشرافية

المعمل المختص / مواد البناء

تقرير الاختبار (Test Report)

بيانات العينة

كود / شهادة الوارد للعينة: -----  
كود المعمل الرئيسي: ٢٠١٩/٤٣٣/٠١١  
مسمى العينة: راسب من محلول كروم  
تاريخ ورود العينة: ٢٠١٩/٤/١٠

عدد الصفحات/ العدد الكلي: (١/١)  
كود المعمل الفرعي: -----  
وصف العينة: بودرة رمادية اللون  
تاريخ إصدار التقرير: ٢٠١٩/٥/٩

مطالب العميل

الفحص المطلوب: تحليل كيميائي كامل - نسبة الكروم  
المواصفة القياسية: -----

بيانات العميل

اسم العميل: أ / سارة إيهاب عبد القادر  
جهة العميل: -----

نتائج الاختبارات

النتيجة	( % )	الاختبارات الكيميائية ( الوحدة )
٠,٠٠٠٠٥	( % )	الكروم السداسي الذائب في الماء ( $Cr^{+6}$ )
٢٨,٥	( % )	الكروم الثلاثي ( $Cr^{+3}$ )
٣,٢	( % )	الكروم الثنائي ( $Cr^{+2}$ )
١٠,١	( % )	أكسيد الكالسيوم ( $CaO$ )
١١,٤	( % )	أكسيد الماغنسيوم ( $MgO$ )
٣٠,٩	( % )	المواد الغير قابلة للذوبان
١,٢	( % )	أكسيد الصوديوم ( $Na_2O$ )
٠,٢٥	( % )	أكسيد البوتاسيوم ( $K_2O$ )
٧,٩	( % )	ثالث أكسيد الكبريت ( $SO_3$ )
٠,١٦	( % )	خامس أكسيد الفوسفور ( $P_2O_5$ )

هذه النتيجة تخص العينة المقدمة ولا تمثل إلا الكمية الممثلة منها العينة ، وتمثيلها لأي كميات أخرى هي مسئولية جهة سحب العينة.  
يحفظ ببقايا العينات بعد اختبارها بمعامل المصلحة لمدة أقصاها شهر من تاريخ الاختبار .  
سريان العمل بتقرير الاختبار لمدة ثلاثة أشهر للعينات العادية ولمدة ستة شهور للعينات من تاريخ إصدار التقرير . ( نهاية التقرير )

المدير العام  
رئيس الإدارة المركزية لمعامل القاهرة

محرر التقرير: راضي  
خلفه

الختم:

تقرير الاختبار يطبع تحت مسئولية مصلحة الكيمياء فقط  
١٩ ٥ ١٢